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Direct Photolysis of Hexacyanoferrate Complexes: Proposed Applications to the Aquatic Environment

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Proposed Applications to the Aquatic Environment

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DIRECT PHOTOLYSIS OF HEXACYANOFERRATE COMPLEXES
Proposed Applications to the Aquatic Environment

by

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FOREWORD

This work represents an effort to characterize the effect of sunlight and various other environmental parameters on the decomposition of iron-cyanide complexes to give hydrogen cyanide. Past work by the authors indicate that hydrogen cyanide can be highly toxic to aquatic organisms. Therefore, this work should provide additional insight for making hazard assessments of iron-cyanide discharges into the environment.

J. David Yount
Acting Director
Environmental Research Laboratory-Duluth

ABSTRACT

The theory and computations described by Zepp and Cline (1977) were experimentally tested in predicting the direct photolysis rates of dilute hexacyanoferrate (II) and (III) solutions in the aquatic environment. Essential information for these calculations includes the quantum yield for the photoreaction, molar extinction coefficients of the complex ions for wavelengths > 295 nm, solar irradiance data used to calculate specific sunlight absorption rates, and the assumption that the photolysis reaction obeys a first-order kinetic rate expression. Direct photolysis rates of the irreversible photochemical reactions are calculated as a function of the time of year, latitude, time of day, meteorological conditions, and depth in natural water bodies. Light of wavelengths < 480 nm is active in the photolysis reactions, and pH, temperature, and concentration all affect the reaction to varying degrees. Assuming first-order kinetics, in which the rate constant was approximately concentration independent within the range of 25-100 µg/l total cyanide, the minimum quantum yields of HCN formation were 0.14 and 0.0023 for the iron (II) and (III) complexes, respectively. These values correspond to minimum, nearsurface, midday half-lives at midsummer of about 18 and 64 min at St. Paul, Minn. The photolysis rate at various fixed depths in a natural water column, when compared with that at the surface, decreases exponentially with depth. It is suggested that the photolysis reactions are enhanced by suspended material in turbid waters because of the forward scattering of light when compared with that theoretically calculated from beam attenuation coefficients. Hexacyanoferrate (II) and (III) solutions of equal initial total cyanide concentration respond photochemically quite differently from one another in solutions prepared with deionized water, but respond in a similar manner for solutions prepared with natural waters. The potentially rapid photodecomposition of iron-cyanides with formation of HCN suggests that this phenomenon may be of toxicological importance under certain environmental conditions.

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SECTION 1

CONCLUSIONS

1. The evaporative loss of HCN from aqueous solutions is directly related to the initial concentration and test temperature. This loss from natural waters is relatively slow when compared with the potential photolysis rate of hexacyanoferrate (II) and (III) complexes for near surface conditions.

2. The colorimetric method for the determination of free cyanide gave the highest estimates of HCN in photodecomposed iron-cyanide solutions. These values were essentially constant at about 1.18 and 1.56 times the HCN determined by the volatilization method, regardless of the extent of photodecomposition, for the hexacyanoferrate (II) and (III) solutions, respectively.

3. Only light of wavelengths less than about 420 and 480 nm are active in the photodecomposition of hexacyanoferrate (II) and (III) complexes, respectively. The maximum absorption of solar radiation by these complexes occurs at about 330 nm for hexacyanoferrate (II) solutions and 330 and 420 nm for hexacyanoferrate (III) solutions.

4. The test pH, temperature, and concentration all have a varying affect on the photolysis reaction of both iron-cyanide complexes.

5. The essentially irreversible photolysis reaction of hexacyanoferrate (II) and (III) complexes can be approximately described by first-order kinetics for concentrations up to 100 µg/l as total cyanide, with minimum quantum yields of HCN formation determined to be 0.14 and 0.0023, respectively.

6. The minimum, near surface, midday direct photolysis half-lives for hexacyanoferrate (II) solutions containing 100 µg/l CN ranged from about 50 min in late fall to a minimum of about 18 min in midsummer at St. Paul, Minn. In comparable hexacyanoferrate (III) solutions the midday half-lives ranged from about 160 min in late fall to a minimum of about 64 min in midsummer.

7. Midday half-lives for the direct photolysis of hexacyanoferrate (II) and (III) complexes near the surface of an aqueous solution and the amplitude of their time of year variation should increase with increasing northern latitude.

8. The intensity of incident collimated sunlight that penetrates natural waters is attenuated through absorption and scattering, thus diminishing the photodecomposition rate of iron-cyanides by reducing the amount of light available.

9. The logarithm of photolysis rate at a specific depth in a water column, as compared to the rate at the surface, was observed to linearly decrease with depth in natural waters.

10. The photolysis reaction in turbid waters is enhanced by suspended material due to forward scattering of light when compared with that theoretically calculated from beam attenuation coefficients.

11. The relatively small concentration of HCN resulting from photolysis of hexacyanoferrate (II) is of minimal toxicological importance below depths of about 50 to 100 cm in most well-mixed natural waters likely to receive this complex as a pollutant.

12. The photodecomposition of hexacyanoferrate (II) and (III) solutions is a direct function of natural light intensity, under varying meteorological conditions.

13. The hexacyanoferrate (II) and (III) complexes photochemically decompose quite differently from one another in deionized water solutions but produce similar amounts of HCN in solutions prepared with natural waters. Because the photolysis reaction of the iron (II) complex was observed to be unaffected by water type, effluents containing these iron-cyanides, when discharged into receiving waters similar to those tested, are expected to respond, with regards to HCN production, like that of the hexacyanoferrate (II) complex.

14. The maximum amount of total cyanide that can be photochemically released as HCN from dilute hexacyanoferrate (II) and (III) solutions prepared with deionized water was determined to be about 85 and 49%, respectively. This indicates that for every mole of iron (II) and (III) complex, each containing 6 moles CN, only 5 and 3 moles of CN, respectively, can be released from the complex anions to form free cyanide through a photolysis reaction in solutions prepared with deionized water.

15. This study indicates that sunlight photodecomposition of iron-cyanides may provide an environmentally important pathway under certain conditions for their conversion into toxic HCN.

SECTION 2

RECOMMENDATIONS

1. Studies are needed to determine the penetration of sunlight into natural waters as a function of light absorption and scattering characteristics for wavelengths greater than 295 nm. These measurements could then be used in mathematical models for predicting photolysis rates as a function of depth.

2. Data collected during this study indicate that hexacyanoferrate complexes may undergo photodecomposition in natural waters which can be of ecological importance under certain circumstances. Since little is known about the behavior of these complexes in natural aquatic environments, research should be initiated to determine the fate of these compounds and HCN in different receiving waters. This work could also be used to test the proposed photolysis model in actual representative polluted waters.

3. A greater understanding of oxidation-reduction reactions involving hexacyanoferrate complexes, as related to redox properties of natural waters, is needed.

4. The toxicity of hexacyanoferrate (II) and (III) complexes to aquatic organisms has been demonstrated to be essentially due to the presence of HCN as derived from the photodecompositon reaction. Therefore, a suitable analytical method for the determination of HCN in the µg/l range is needed in order to determine the actual adverse effects of cyanide on aquatic organisms in waters receiving iron-cyanide wastes.

5. Nearly all of the lethal and sublethal effects of HCN on aquatic organisms have been derived from continuous and constant toxicant exposure tests. However, it is reasonable to expect HCN concentrations in most natural waters to fluctuate because of intermittent waste discharge, and due to the loss of cyanide and limited formation of HCN from the photodecomposition of iron-cyanides at night. Therefore, additional information on the toxicity of fluctuating HCN concentrations is needed in order to more realistically establish the adverse effects of cyanide on aquatic populations in natural waters.

SECTION 3

INTRODUCTION

Appreciable amounts of ferro- and ferricyanides (i.e., hexacyanoferrate (II) $Fe(CN)_6^{4-}$, and (III) $Fe(CN)_6^{3-}$) may occur in effluents from color film photographic processes, electrostatic conversion washes, the manufacture of iron and steel, the cracking of oil, and from plants which manufacture these iron salts. It has also been established that the toxicity to many aquatic organisms of aqueous solutions of various simple cyanides and metallocyanide complexes is determined virtually alone by the concentration of undissociated molecular HCN and not by the concentration of the cyanide ion (CN^-) or of most metallocyanide anions (Doudoroff, 1976; Broderius et al., 1977). Hydrocyanic acid (HCN) is formed in hexacyanoferrate (II) and (III) aqueous solutions mainly through photodecomposition of the iron-cyanide anions, which are otherwise highly stable and relatively nontoxic, and through hydrolytic reaction with water of the cyanide ions so liberated. Fish kills in a New York stream (Burdick and Lipschuetz, 1950) and a Japanese river (Kobayashi and Mori, 1973) were associated with the discharge of iron-cyanides in industrial effluents at concentrations less than generally accepted as nonlethal. The rapid development of a toxic situation was demonstrated to result from photodecomposition of the iron-cyanides by bright sunlight and release of free cyanide (i.e., HCN + CN^-). Similar findings were reported by Myers (1950) for seepage from a ferromanganese blast furnace and for chemicals from photographic processing by West (1970) and Terhaar et al. (1972). The influence of sunlight and pH on degradation of iron-cyanides in a polluted natural water was reported by Kongiel-Chablo (1966).

The photochemical behavior of potassium ferro- and ferricyanide in aqueous solutions and the kinetics of their decomposition and reverse reaction has been investigated extensively for various irradiation wavelengths in the absorption spectral region. Solutions of both complexes when kept in the dark or in diffused light are stable but when exposed to light of certain wavelengths, decomposition occurs with the formation of aquopentacyanoferrates and reduction of ferricyanide to ferrocyanide. According to Ohno and Tsuchihashi (1965) and Ohno (1967), irradiation of aqueous hexacyanoferrate (II) solutions with light of 366 nm causes a ligand substitution reaction yielding aquopentacyanoferrate (II) ($Fe(CN)_5 \cdot H_2O^{3-}$) and cyanide ion. Light of 253.7 nm resulted in a photo-oxidation reaction producing hexacyanoferrate (III) and reducing species. Upon continued irradiation of ferrocyanide solutions with wavelengths longer than 300 nm, Fe^{2+} and HCN are also formed and the pH slowly increases during irradiation, as a result of the hydrolysis of the cyanide ions produced, and after some time tends to reach a constant value (Asperger, 1952). When the light is removed, the reaction is apparently reversed under certain circumstances and the original pH restored if the irradiation has not been too prolonged. The reverse reaction apparently depends on the iron-cyanide concentration and is caused by

a slower secondary reaction between the aquo salt formed and the parent compound (MacDiarmid and Hall, 1953). Asperger et al. (1960) stated that the reaction is apparently reversible only when no appreciable decomposition of the aquopentacyanoferrate (II) ion occurred. Under prolonged irradiation on aerated and relatively concentrated solutions, $Fe(OH)_3$ (in alkaline solutions) and Prussion blue (in acid solutions) are formed (Balzani and Carassiti, 1970).

A mechanism for the photodecomposition of potassium ferrocyanides can be represented according to Asperger (1952) and Mitra et al. (1963) by the primary reaction

$$Fe(CN)_6^{4-} \rightleftarrows Fe(CN)_5^{3-} + CN^-$$

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

$$\underline{Fe(CN)_5^{3-} + H_2O \rightleftarrows Fe(CN)_5 \cdot (H_2O)^{3-}}$$

$$Fe(CN)_6^{4-} + 2\ H_2O \rightleftarrows Fe(CN)_5 \cdot (H_2O)^{3-} + HCN + OH^- \qquad (1)$$

Asperger (1952) and Balzani and Carassiti (1970) have stated that in the second phase the thermally and photochemically unstable $Fe(CN)_5 \cdot (H_2O)^{3-}$ is decomposed by prolonged exposure to light with a progressive photosubstitution reaction with increase in pH and release of Fe^{2+} plus CN^- ions. In the presence of oxygen $Fe(OH)_3$ can be formed.

There are a number of publications on the photochemistry of aqueous ferricyanide solutions, but Balzani and Carassiti (1970) stated that the complicated photochemical behavior of this complex is not yet completely understood. Moggi et al. (1966) showed that the photochemical behavior of $Fe(CN)_6^{3-}$ was qualitatively the same regardless of the wavelength of irradiation (254, 313, or 405 nm light). Spectral changes suggested that $Fe(CN)_5 \cdot (H_2O)^{2-}$ was formed as the main product with the hydrolysis step probably proceeding according to

$$2Fe(CN)_6^{3-} + 2H_2O \rightleftarrows 2Fe(CN)_5 \cdot (H_2O)^{2-} + 2CN^- \qquad (2)$$

In the dark the complex slowly underwent an oxidation-reduction reaction which was accelerated by light and the presence of CN^- according to

$$2Fe(CN)_5 \cdot (H_2O)^{2-} + CN^- + 2OH^- \rightleftarrows 2Fe(CN)_5 \cdot (H_2O)^{3-} + CNO^- + H_2O \qquad (3)$$

with the overall hydrolysis reaction

$$2Fe(CN)_6^{3-} + H_2O + 2OH^- \rightleftarrows 2Fe(CN)_5 \cdot (H_2O)^{3-} + CN^- + CNO^- \qquad (4)$$

Upon irradiation by light the rates of the above reactions (equations 2 and 3) increase, Fe^{2+} ions are formed, and the pH of the solution initially increases.

Balzani and Carassiti (1970) stated that in addition to a photosubstitution reaction, a direct photoreduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_5 \cdot (H_2O)^{3-}$ could occur. The oxidation-reduction reaction of hexacyanoferrate (III) ions was demonstrated by Adamson (1952) to be rapid whenever the process involves a simple electron transfer and to be slow and of complex mechanism if such a step cannot occur. The major product of the rapid reaction was suggested to be hexacyanoferrate (II) ion (i.e., $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$ 0.36 volt) rather than an aquocyanide and no intermediate ions with a different number of coordinate cyanide groups is involved. Since the nature and yields of the products for photochemical reactions involving iron-cyanides are not completely defined, the overall chemical changes and the reaction mechanisms are not well established.

The first step in direct photolysis is the absorption of a light quantum (photon) resulting in an electronically excited state of the molecule. Therefore, only radiant energy which is absorbed by a molecule can be effective in producing photochemical changes. Each light quantum absorbed activates one molecule so that the efficiency of the photochemical process can be represented by the quantum yield. This yield is defined by the ratio of the number of molecules undergoing chemical reaction divided by the number of photons absorbed by the reactants. In most cases this is experimentally measured by the rate of the chemical reaction divided by the number of quanta absorbed per second (Balzani and Carassiti, 1970).

According to a review by Balzani and Carassiti (1970), the reported quantum yields for the photodecomposition of hexacyanoferrate (II) and (III) complexes, as obtained by various authors using different experimental conditions and techniques, are generally in disagreement. Upon irradiation of aqueous hexacyanoferrate (II) solutions with wavelengths of about 313 or 365 nm, the ligand substitution quantum yield for aquopentacyanoferrate (II) formation was reported to be 0.1 using pH measurements in neutral unbuffered solutions (Carassiti and Balzani, 1960) and 0.44 for a 0.5 M solution at pH 9.9 (Emschwiller and Legros, 1954). A value of 0.89 was determined from the amount of $Fe(CN)_5 \cdot (H_2O)^{3-}$ formed at pH 4.0 (Ohno and Tsuchihashi, 1965). The quantum yield was reported by Balzani and Carassiti (1970) to be almost independent of $Fe(CN)_6^{4-}$ concentration, temperature, light intensity, and pH in the range 7-10. However, Ohno (1967) stated that the quantum yield decreased with an increase in the hexacyanoferrate (II) concentration.

The quantum yields for the formation of $Fe(CN)_5 \cdot (H_2O)^{2-}$ and $Fe(CN)_6^{4-}$ from irradiation of hexacyanoferrate (III) solutions with light of 365 nm were reported by Balzani and Carassiti (1970) to be 0.009 and 0.014 at pH 4, and 0.0065 and approximately 0.018 at pH 10, respectively. However, these results should be taken with reservation since questionable procedures were used in their determination (Balzani and Carassiti, 1970).

The lack of correlation between photodecomposition tests conducted with natural and artificial light can be due to the difference in the ultraviolet spectral energy distribution and intensity of sunlight, and the various artificial light sources. Because solar radiation at the earth's surface has negligible intensity at wavelengths less than about 295 nm (Bener, 1972), the

chemical of interest must have appreciable absorptivity at greater wavelengths if significant photoreaction is to occur in sunlight. Most past studies of the photodecomposition of hexacyanoferrate (II) and (III) complexes were not prompted by environmental considerations, and thus much of the information derived from them cannot be extrapolated to natural water environments. The primary purpose of this study was to determine the photochemical response of iron-cyanides under natural light conditions in natural bodies of water, both near the surface and as a function of depth. Such a study allowed us to evaluate the relative importance of these compounds as sources of toxic hydrocyanic acid (HCN) in natural waters. The approach used for predicting the photochemical decomposition by solar radiation of such compounds in aquatic environments was based on principles and equations described by Zepp and Cline (1977).

SECTION 4

MATERIALS AND METHODS

ANALYTICAL METHODS

Aliquots of hexacyanoferrate (II) and (III) solutions were tested periodically for free cyanide (i.e., $HCN + CN^-$) by the pyridine-pyrazolone colorimetric method (APHA, 1971). Molecular HCN concentrations were calculated from free cyanide and pH measurements, and dissociation constants derived from $pK_{HCN} = 3.658 + 1662/T$ where T is temperature in degrees Kelvin (Broderius and Smith, 1979). This procedure worked satisfactorily for both the deionized and natural water solutions when appropriate corrections were made. A method similar to that proposed by Broderius and Smith (1977) for the determination of H_2S and by Broderius (1973) for studies with metallocyanide complexes was incorporated for the direct determination of molecular HCN in the µg/l range. This procedure utilizes a glass bead concentration column coated with 0.1 N NaOH for collecting displaced HCN, which is determined colorimetrically. The separation of HCN from a sample by means of displacement with N_2 bubbled through the solution does not upset the chemical equilibrium involving the various cyanide forms.

Turbidity was measured on well-shaken samples with a Hach model 2100A turbidimeter* and was reported in Nephelometric Turbidity Units (NTU). Total and filterable residue, pH, and dissolved oxygen were also determined according to standard procedures (APHA, 1971).

Light was measured with a LI-COR model LI-185 quantum meter**, a LI-192S underwater quantum sensor with a spectral response based on photon absorption between 400 and 700 nm, and a mv recorder. For experiments relating different meteorological conditions with photolysis rate, these measurements were integrated with exposure period to determine change in energy associated with radiation incident to test solutions.

Molar extinction coefficients were determined with a Beckman DB-GT spectrophotometer from electronic absorption spectra of the hexacyanoferrate (II) and (III) complex anions in deionized water. The light from the spectrophotometer was insufficient to cause any measurable photochemical reaction.

TEST PROCEDURES AND APPARATUS

All chemicals were of reagent-grade quality and were used without additional purification. Iron-cyanide solutions were usually prepared by

---

* Hach Chemical Company, Ames, Iowa.
**Lambda Instruments Corporation, Lincoln, Nebraska.

weighing out potassium salts immediately before use and dissolving in deionized water saturated with dissolved oxygen. Appropriate further dilution under laboratory light gave the desired concentrations. Iron-cyanide solutions with concentrations of 25 to 200 µg/l as total CN were generally used. The pH in solutions prepared with potassium iron-cyanide and deionized water was maintained with phosphate or borate buffer concentrations of about 10^{-3} M. Nearly all test solutions prepared with deionized water were buffered at pH 7.8.

In photochemical experiments the reaction cells through which the light travels to reach the dissolved reactant must be transparent to the exciting radiation. This was accomplished by conducting the exposure experiments in open vessels or in tightly sealed tubes which were irradiated by sunlight on the roof of our laboratory in St. Paul, Minn. (latitude 45° N, longitude 93.2° W). The test solutions were exposed to sunlight in 25 x 150 mm Teflon lined screw-cap Pyrex test tubes (Corning No. 9826) unless stated otherwise. A series of tubes for each concentration was filled to the brim and submerged in 40 mm of deionized water in a water bath thermostatically controlled, usually at 20 $\pm$ 0.1°C. The tubes were positioned horizontally above a black background in a shallow tray to minimize reflected light, or for field experiments at various fixed depths in a natural water column. It was determined that the photolysis rates for solutions prepared with deionized water and exposed in test tubes were not significantly different ($P = 0.05$) from those determined for 8 l of test solution in an open 2-gal Pyrex acid battery jar (21 cm diameter x 25 cm high, Corning 6942) blackened on the inside and tilted directly towards the sun's rays. Therefore, change in photolysis rates due to internal reflection of sunlight and slight absorption of active light wavelengths in the Pyrex test tubes submerged in water appeared to be insignificant factors. Losses of HCN to the atmosphere from open vessels were also minimal during the relatively short exposure periods. The concentration of free cyanide determined in an open vessel was the same for solutions which were stirred occasionally or undisturbed.

The shadowing effect on the test solutions by the walls of the test jars during low sun angles prevented using them in an upright position for the determination of actual photolysis rates. However, the jars can be used for comparative type experiments. To determine the effect of turbidity and materials dissolved in natural waters on the photodecomposition reaction, hexacyanoferrate (II) and (III) solutions in test jars were exposed to natural light filtered by about 40 mm of various solutions placed in open Pyrex filters (27 cm square x 5 cm high) placed directly over the jars. The photolysis rates calculated for these iron-cyanide solutions were divided by the rates determined for comparable solutions subjected for the same exposure period but in jars under light that had been filtered through 40 mm of deionized water. In this way relative photolysis rates were calculated.

During the photolysis experiments, samples from test jars were frequently taken or test tubes from a certain series were removed periodically and analyzed spectrophotometrically for free cyanide. Control solutions kept in the dark showed no measurable formation of free cyanide during the exposure period of similar solutions. Based on the fraction of hexacyanoferrate (II) and (III) that disappeared, as measured by the formation of free cyanide or

HCN, photolysis rate constants and half-lives were calculated assuming first-order kinetics.

COMPUTATIONAL APPROACH

The rate of HCN loss from open acid battery jars is proportional to the remaining hydrogen cyanide concentration at any time. According to Palaty and Horokova-Jakubu (1959), this loss can be expressed by a first-order rate equation. Therefore, the half-life, or time required to reduce the original concentration of hydrogen cyanide to one-half, is given by the equation

$$t_{\frac{1}{2}} = \frac{0.693}{k} \text{ or } t_{\frac{1}{2}} = \frac{0.693\ t}{\ln(C_o/C)} \qquad (5)$$

where C_o is the initial and C the final HCN concentration after time t. If $\ln C_o/C$ calculated from the experimental data is plotted as a function of HCN removal time, equation (5) is an expression of a straight line passing through the zero coordinates. The slope of the line equals the rate constant ($k=\ln(C_o/C)/t$) of HCN removal. The value of k is a function of the factors affecting HCN loss and consequently it can be used to characterize and compare these effects.

Quantitative calculations of direct sunlight photolysis rates and half-lives were made from quantum yields and electronic absorption spectra of hexacyanoferrate (II) and (III) aqueous solutions assuming first-order kinetics. Equations defining the intensity and path lengths of direct and sky radiation in air and water as described by Zepp and Cline (1977) were employed. With this approach, photolysis rates under average intensities derived from full sunlight and the whole sky on cloudless days were calculated as a function of latitude and longitude, time of year, time of day, depth in a water body, and other influencing parameters. The input data required to calculate the theoretical photolysis rates are

(1) molar extinction coefficients of the hexacyanoferrate (II) and (III) complex anions at wavelengths > 297.5 nm;

(2) the attenuation coefficient or absorbance per cm for the reaction medium (a refractive index of 1.34 is assumed);

(3) the quantum yield for the direct photolysis reaction;

(4) the angular height of the sun as determined from the solar declination, solar right ascension, and sidereal time for the date of interest as obtained from the American Ephemeris and Nautical Almanac;

(5) the latitude and longitude; and

(6) the average atmospheric ozone layer thickness that pertains to the season and location of interest (a value of 0.30 cm was assumed - London, 1963).

The average sunlight photolysis rate at a certain wavelength (λ) is proportional to the quantum yield (ϕ_λ) for the reaction of the weakly absorbing system. The kinetic expression for this formula as discussed by Zepp and Cline (1977) is

$$-\left(\frac{d[P]}{dt}\right)_\lambda = \phi_\lambda \; k_{a_\lambda} [P] \tag{6}$$

where [P] is the hexacyanoferrate (II) or (III) concentration in moles/liter and $k_{a\lambda}$ is the specific sunlight absorption rate as a function of wavelength. The $k_{a\lambda}$ term is equal to the wavelength specific average rate of light absorption per unit volume ($I_{a\lambda}$) times the molar extinction coefficient of the iron-cyanide (ε_λ) divided by the attenuation coefficient of the water body (α_λ) times a constant (j, 6.02×10^{20}) which converts the intensity expressed in photons $cm^{-2}s^{-1}$ into units compatible with [P] (Zepp and Cline, 1977). Assuming that the quantum yield for the photolysis reaction in solution is not wavelength dependent then the rate expression is

$$-\left(\frac{d[P]}{dt}\right) = \phi k_a [P] \tag{7}$$

where k_a equals the sum of the $k_{a\lambda}$ values integrated over all wavelengths of sunlight absorbed by the reactants. This expression conforms to a first-order rate equation in which the photolysis rate constant (ϕk_a) is expressed in units of reciprocal time. The value of k_a changes during the day because the surface spectral flux distribution of solar radiation is a function of the solar zenith angle. For natural waters k_a is also a function of competitive light absorption by the water itself along with other absorbing materials and light scattering. Because in most natural waters attenuation due to light scattering is less important than that due to absorption, scattering was initially ignored in the following computations. Surface reflection and scattering from water bodies was also ignored because it is small (about 5 to 6 percent) for most solar zenith angles (Hutchinson, 1957).

For a first-order reaction the half-life ($t_{1/2}$), or time required for one-half of a compound to react, is independent of the initial concentration and can be expressed by

$$t_{1/2} = \frac{0.693}{\phi k_a} \text{ or } t_{1/2} = \frac{0.693\ t}{\ln(P_o/P)} \tag{8}$$

where t is the time of exposure, and P_o is the initial iron-cyanide concentration expressed as HCN with that after exposure (P) equal to P_o minus the determined HCN concentration. The half-lives represent the period of time required to decompose the iron-cyanides with release of half the HCN that can be potentially formed from the specific complexes. The photolysis rate constant (ϕk_a) can be calculated from the expression $\ln(P_o/P)/t$.

A computer program written in Fortran IV, that uses the above mentioned theory and equations to compute direct photolysis rates, is available on request from the Environmental Research Laboratory-Athens, Georgia, U.S. Environmental Protection Agency (Zepp and Cline, 1977).

SECTION 5

RESULTS AND DISCUSSION

VOLATILIZATION OF HCN

The volatilization of HCN from 8 l sodium cyanide solutions prepared with deionized water and placed in 2 gal acid battery jars was determined in the laboratory as a function of temperature and concentration. This rather slow loss of cyanide, determined from 6 hr exposure periods, is apparently not independent of the initial concentration as indicated by the variation in the first-order rate constants in Table 1. This correlation between rate constant for HCN loss and initial concentration implies that the evolution of HCN from an open aqueous solution does not follow the first-order kinetics as anticipated. However, from the limited number of tests conducted, it is concluded that the loss is approximately first-order, especially when one considers the possible analytical error introduced into the determinations for solutions with the lowest initial cyanide concentrations.

At a given initial cyanide concentration a decrease in test temperature resulted in higher residual cyanide concentrations. This is indicated by a reduction with decreasing temperature in the rate constant for HCN loss to the atmosphere from the surface of comparable solutions. Over the temperature range 10 to 25° C, this decreased rate is approximately a linear function of temperature such that for a 10° C decrease the rate constant is reduced by about 55%. Experiments conducted with solutions placed in jars on the roof of our laboratory demonstrated that the rate of HCN loss was about twice that determined in the laboratory. This increase is most likely a result of increased loss due to wind action, since it was demonstrated that HCN was not subjected to photolysis by natural light. Also, solutions placed on the roof and loosely covered with a sheet of glass showed approximately the same rate of HCN loss when compared with similar solutions in the laboratory.

Since the loss of HCN from a solution into the atmosphere is through the phase borderline, the rate of cyanide decrease is a function of the surface area to solution volume ratio. For our containers with perpendicular walls the HCN removal rate is inversely proportional to the solution depth. Thus the time required for the removal of HCN to 1/2 its original concentration is directly proportional to the solution depth, since the same type of container and solution volume was used in all HCN rate loss experiments, temperature and initial concentration are the only variables for which a comparison of HCN removal can be made.

The total loss of cyanide from natural waters occurs not only by volatilization into the atmosphere but also through chemical reactions and biological oxidation to ammonia and CO_2. The above calculated rates represent only minimal losses since the oxidative loss is negligible in

TABLE 1. RATE OF HCN LOSS FROM SODIUM CYANIDE SOLUTIONS PREPARED WITH DEIONIZED WATER AND IN OPEN CYLINDRICAL JARS UNDER LABORATORY CONDITIONS*

Initial free cyanide conc. (µg/l CN)	Temperature (°C)			
	10	15	20	25
	Rate Constant, $k(hour^{-1})$			
25	0.00624	0.0139	0.0194	0.0257
50	0.0103	0.0117	0.0225	0.0263
100	0.0136	0.0135	0.0215	0.0299
200	0.0149	0.0173	0.0254	0.0315
	Half Life, $t_{1/2}$ (hour)			
25	111.0	49.7	35.8	27.0
50	67.3	59.4	30.8	26.3
100	50.8	51.5	32.2	23.2
200	46.5	40.1	27.3	22.0

*Test solution pH was about 7.9.

deionized water solutions as well as the loss through agitation since the solutions were unstirred.

Lure and Panova (1964) determined that for river water test solutions initially containing 10 to 25 mg/l CN and exposed in open vessels, the concentration of cyanide during standing declines after 7 days to about 10% of the original with the complete disappearance of cyanide occurring in 10-12 days. These authors concluded that in the natural water they investigated, the loss of cyanide by volatilization is the most significant of the means of HCN decline.

The rate of HCN loss has been demonstrated to depend on temperature but Palaty and Horokova-Jakubu (1959) observed that the intensity of agitation and ratio of the solution volume to surface area are also very important factors. In fact, they determined the removal rate in vigorously air-agitated solutions to be one order of magnitude greater (12 to 14 times) than the nonagitated solutions. However, even though the decomposition of simple cyanides dissolved in natural and deionized water occurs differently, it is likely that the rapid loss of HCN under the most favorable circumstances is still considerably slower than the formation of HCN from photolysis of hexacyanoferrate (II) and (III) complexes for midday and near surface conditions.

FREE CYANIDE AND HCN DETERMINATIONS

It has been assumed by previous workers (Burdick and Lipschuetz, 1950) that the pyridine-pyrazolone method for the measurement of free cyanide does not upset the chemical equilibria by liberating cyanide from the hexacyanoferrate complex ions or intermediate photolysis forms. Comparison of the direct vapor phase method and the indirect colorimetric methods for the determination of HCN (Broderius, 1973) demonstrated that the indirect pyridine-pyrazolone method gives a relatively high estimate of free cyanide in iron-cyanide solutions. This may be due to some cyanide which is liberated from the hexacyanoferrate complex ions or intermediate photolysis forms by the pyridine-pyrazolone method. In five tests with each complex, however, the ratios between HCN concentrations determined by the direct vapor phase equilibration procedure and those estimated by the indirect colorimetric method were relatively constant, regardless of the degree of decomposition, at about 84.6% and 64.2% for the hexacyanoferrate (II) and (III) solutions, respectively (Table 2). Therefore, the indirect colorimetric method for the estimation of HCN concentrations can be used when the relative (normalized) photolysis rates of hexacyanoferrate (II) and (III) solutions exposed to natural light are determined. When the proper correction is made the results from the indirect colorimetric method can also be used to determine the actual photolysis rate of these complexes as indicated by HCN formation.

KINETICS OF PHOTODECOMPOSITION

Molar Extinction Coefficients

The electronic absorption spectra of freshly prepared and dilute potassium $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ aqueous solutions were measured in the wavelength

TABLE 2. THE HCN CONCENTRATION ESTIMATED BY THE INDIRECT COLORIMETRIC METHOD AND THAT DETERMINED BY THE DIRECT VAPOR PHASE EQUILIBRATION PROCEDURE FOR HEXACYANOFERRATE (II) AND (III) SOLUTIONS EXPOSED TO SUNLIGHT AND INITIALLY CONTAINING 100 µg/l CN*

Test	Determined HCN concentration, µg/l: A Indirect colorimetric method	B Direct vapor phase equilibration method	Percentage B of initial total cyanide	Ratio B/A
		Ferrocyanide solutions		
1	33.9	29.9	29.9	88.2
2	38.8	31.4	31.4	80.9
3	60.4	51.2	51.2	84.8
4	83.1	68.9	68.9	82.9
5	98.2	84.8	84.8	86.4
			mean	84.6
				±2.9
		Ferricyanide solutions		
1	25.7	17.2	17.2	66.9
2	45.2	27.7	27.7	61.3
3	47.2	31.7	31.7	67.2
4	60.9	37.5	37.5	61.6
5	64.8	41.4	41.4	63.9
			mean	64.2
				±2.8

*Test temperature was 25° C and pH 7.9.

region close to the strong ultraviolet absorption bands. As seen in Figure 1, these complexes are photosensitive at wavelengths <420 nm for the ferro and <480 nm for the ferri ions. Therefore, photolysis rates of these complexes would be expected to reflect fluctuations in intensity of the shorter wavelength component of sunlight. The molar extinction coefficients (ε) (Table 3) derived from the absorption spectra of freshly prepared aqueous solutions of potassium $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ (approximately 10^{-3} M) agreed closely with those reported by Ibers and Davidson (1951), Adamson (1952), and Asperger (1952). A possible reaction product, $Fe(CN)_5 \cdot (H_2O)^{3-}$, has also been reported to absorb photoactive spectral light (Asperger, 1952). However, this product is a transient intermediate and since absorption spectra of reaction solutions were quite similar in shape and reductions in these spectra were proportional to the degree of decomposition, it was assumed that the predominant cyanide components contributing to the total absorption were the hexacyanoferrate (II) and (III) ions.

Specific Sunlight Absorption Rate

The rate of a photochemical reaction in an aqueous solution is dependent upon the solar spectral irradiance at the solution surface, radiative transfer from air into the solution, and the transmission of sunlight in the solution. Through absorption by components in the atmosphere, the intensity of sunlight is decreased such that the ultraviolet and visible region decreases with decreasing wavelength so that essentially no light is transmitted to the earth's surface at wavelengths <295 nm (Bener, 1972). Molar extinction coefficients of hexacyanoferrate (II) and (III) ions can be coupled with actinic irradiance data of Leighton (1961) and Bener (1972) to calculate the specific rate of sunlight absorption (k_a) (Zepp and Cline, 1977). The magnitude of these rates depends upon the degree of spectral overlap between the electronic absorption spectra and the spectrum of sunlight at the earth's surface. The specific sunlight absorption rates ($k_{a\lambda}$) of hexacyanoferrate (II) and (III) complexes were computed as a function of wavelength for shallow depths and apply to midsummer and midday at latitude 40° N. Only wavelengths of less than about 480 nm are photometrically important (Figure 2). The maximum interaction with solar radiation occurs at about 330 nm for ferrocyanide solutions and at 330 nm and 420 nm for ferricyanide solutions. The ratio of integrated $k_{a\lambda}$ values (k_a) for the wavelength region of 297.5 - 490 nm indicates that the sunlight absorption rate constant for ferricyanide is about 17 times larger than that for ferrocyanide (Figure 2).

Properties of Photochemical Reaction

The photolysis of hexacyanoferrate (II) and (III) complexes in solutions of certain initial total cyanide concentrations follows first-order kinetics as indicated by typical linear regression correlation coefficients in Table 4. These values are for the relationships between midday exposure period and calculated log iron-cyanide concentration for solutions with initial complex concentrations up to 200 µg/l as total cyanide. It has been proposed that the reaction is reversible in darkness (Asperger et al., 1960). However, determinations of the amount of released cyanide that is recombined or lost showed that the reaction is irreversible in the dark for ferricyanide solutions, but

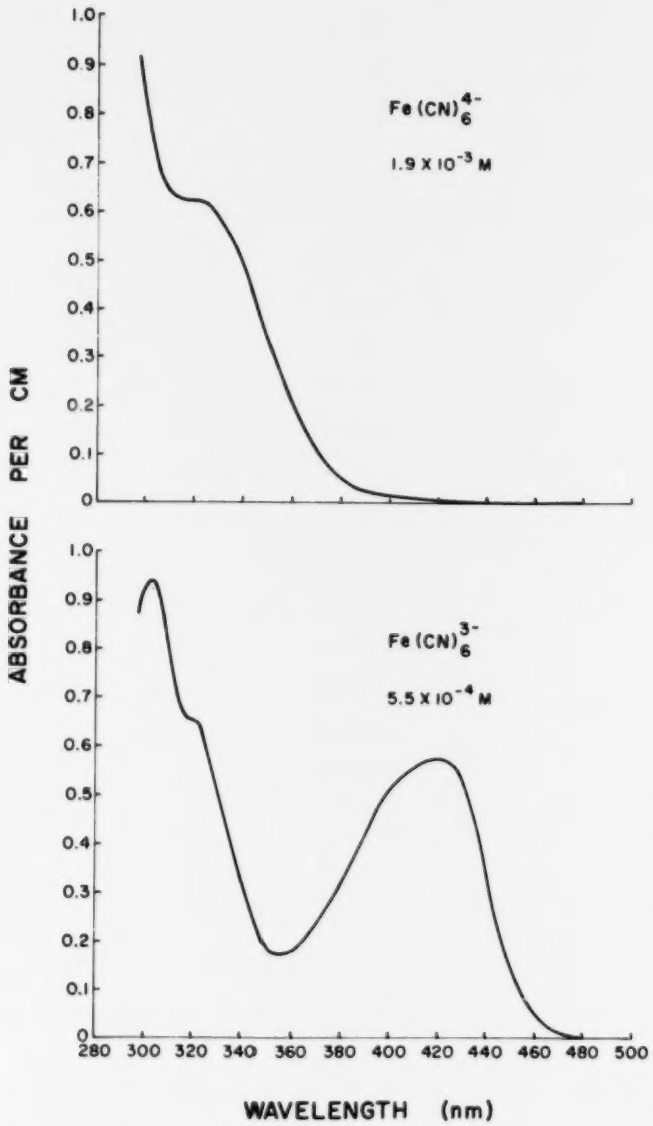

Figure 1. Electronic absorption spectra of hexacyanoferrate (II) and (III) solutions.

TABLE 3. MOLAR EXTINCTION COEFFICIENTS OF HEXACYANOFERRATE (II) AND (III) SOLUTIONS

Wavelength (nm)	Extinction coefficient, liter/mole-cm	
	$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$
297.5	483.7	1589
300.0	428.5	1673
302.5	387.9	1710
305.0	363.2	1677
307.5	346.9	1575
310.0	335.3	1410
312.5	330.6	1279
315.0	329.0	1215
317.5	328.5	1193
320.0	328.5	1195
323.1	326.4	1175
330.0	309.5	938
340.0	252.7	571
350.0	174.8	334
360.0	105.3	336
370.0	55.8	434
380.0	25.8	577
390.0	11.0	770
400.0	5.3	945
410.0	2.6	1007
420.0	1.6	1053
430.0	1.6	932
440.0	1.0	597
450.0	1.0	261
460.0	0.5	80
470.0	0.5	18
480.0	0.0	4
490.0	0.0	0

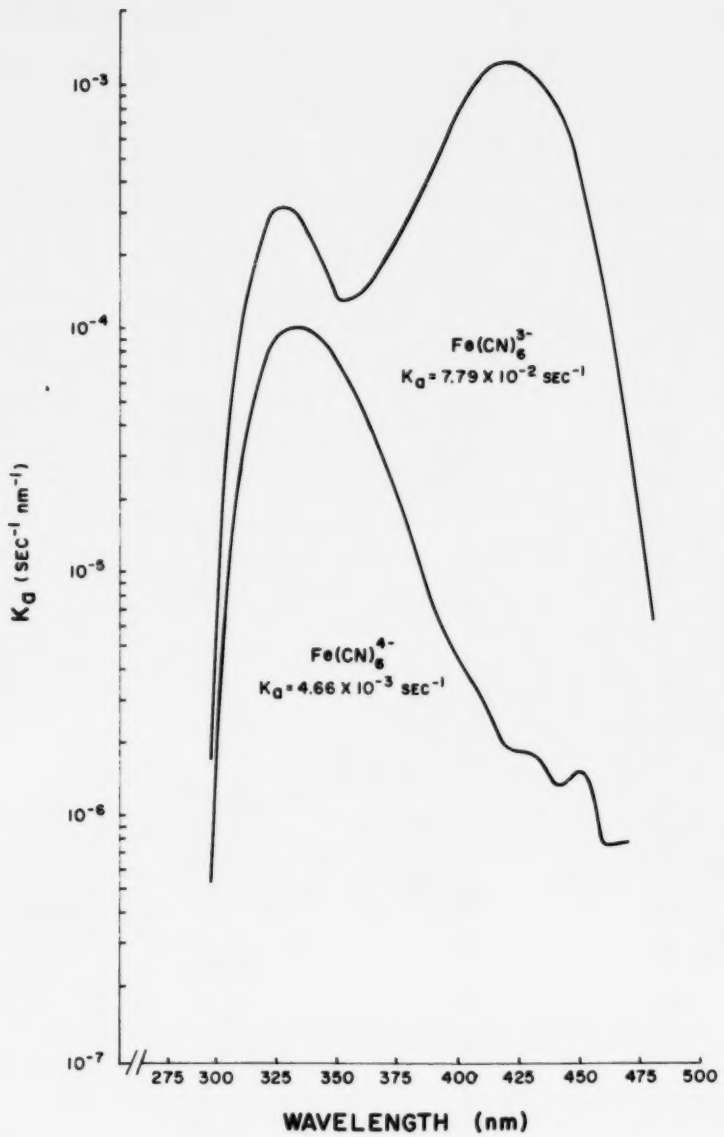

Figure 2. Specific sunlight absorption rates of hexacyanoferrate (II) and (III) complexes as a function of wavelength at midday and mid-summer, latitude 40° N.

TABLE 4. THE LINEAR RELATIONSHIP BETWEEN EXPOSURE PERIOD (X) NEAR MIDDAY FOR DIFFERENT METEOROLOGICAL CONDITIONS AND CALCULATED LOG IRON-CYANIDE CONCENTRATION (Y), FOR SOLUTIONS WITH INITIAL COMPLEX CONCENTRATIONS UP TO 200 µg/l AS TOTAL CYANIDE, AS INDICATED BY THE REGRESSION CORRELATION COEFFICIENT

Total cyanide, µg/l CN	Exposure period, min	Determined HCN concentration, µg/l CN	Calculated iron-cyanide concentration as µg/l CN	Linear correlation coefficient, r
		$Fe(CN)_6^{4-}$		
25	0	0	25.00	
	15	4.95	20.05	0.962
	45	13.0	12.0	
	75	15.1	9.9	
50	0	0	50.0	
	15	11.2	38.8	0.999
	45	27.6	22.4	
	75	36.2	13.8	
100	0	0	100.0	
	15	36.8	63.2	0.992
	45	69.4	30.6	
	75	82.7	17.3	
200	0	0	200.0	
	15	68.4	131.6	0.990
	45	128.8	71.2	
	75	156.3	43.7	
		$Fe(CN)_6^{3-}$		
25	0	0	25.00	
	15	1.87	23.13	
	45	5.87	19.13	0.972
	75	7.96	17.04	
	135	10.8	14.2	
50	0	0	50.00	
	15	4.46	45.54	
	45	11.5	38.5	0.981
	75	16.2	33.8	
	135	22.3	27.7	
100	0	0	100.00	
	15	8.22	91.78	
	45	21.6	78.4	0.986
	75	31.5	68.5	
	135	43.9	56.1	
200	0	0	200.00	
	15	28.9	171.1	
	45	63.7	136.3	0.897
	75	82.0	118.0	
	135	94.9	105.1	

is slightly reversible though incomplete for ferrocyanide solutions that have undergone only minimal decomposition. After prolonged exposure the reaction becomes irreversible, even for ferrocyanide solutions.

The photolysis reactions for both iron-cyanide complex solutions initially containing 100 µg/l CN were virtually unaffected by dissolved oxygen in the range 2 - 8 mg/l. There was a moderate effect of pH on the photolysis reactions with the rates increasing with a decrease of test pH over the range 9.0 - 6.6. The relative rates normalized to that determined at pH 6.6 decreased to about 0.84 and 0.70 at pH 9.0 for the ferri- and ferrocyanide solutions, respectively. The decrease in relative rate with increase in pH is linear over the pH range tested for ferricyanide solutions but decreases in a linear manner only from pH 6.6 to about 8.0 and then remains fairly constant to pH 9.0 for ferrocyanide solutions.

The photochemical reaction rate for iron-cyanide solutions initially containing 100 µg/l CN and at pH 7.8 was measured at 5.6, 12.1, and 23.5° C. The slight negative temperature relationship between the relative photolysis rate (Y) normalized to the rate determined at 23.5° C, as a function of test temperature in ° C (X), can be represented by

$$\text{Log } Y = -0.104 + 0.00464\ X \quad (r = 0.962)$$

and $$\text{Log } Y = -0.136 + 0.00574\ X \quad (r = 0.999)$$

for hexacyanoferrate (II) and (III) solutions, respectively. Balzani and Carassiti (1970) stated that this observed temperature dependence may be due to secondary thermal reactions which contribute to the overall quantum yield.

Varying the initial concentration of iron-cyanide salt affected the photodecomposition rate constant. The dependence of this constant on concentration demonstrates, according to Asperger (1952), that the decomposition is due not only to the light energy, but also to collision of molecules. Therefore, photolysis of the hexacyanoferrate (II) and (III) complexes is not truly first-order. For practical purposes, however, we can assume that the reactions follow first-order kinetics for complex concentrations that are likely to be found in natural waters. The relative photolysis rate constants normalized to those determined for solutions at 20° C with an initial total cyanide concentration of 25 µg/l CN and as a function of the average iron-cyanide concentration during the rate determination period are represented in Figure 3. The pH of all solutions was about 7.8. The rate constants of the decomposition reaction decrease with increasing initial cyanide complex concentration up to some apparent limiting concentration. The relative photolysis rate constant normalized to that determined for 25 µg/l total cyanide (Y) was a function of average hexacyanoferrate (II) concentration (X) up to 1000 µg/l CN and can be represented by the empirical expression, $Y = 2.099\ X^{-0.2220}$ ($r = -0.954$). For hexacyanoferrate (III) solutions the above relationship can be represented by $Y = 1.390\ X^{-0.1538}$ ($r = -0.904$). Photolysis rates were determined for comparable hexacyanoferrate (II) and (III) solutions prepared with deionized water and exposed to the same light conditions. The ratio of these rates for ferro- to ferricyanide solutions over the initial total cyanide concentration range of 25 - 200 µg/l CN averaged 2.05 $\pm$ 0.32 for 32 such comparisons. However, the rate of change in photolysis rate constants (Figure 3) is such that at initial total cyanide concentrations of approximately 2.0 mg/l CN and greater the decomposition rate

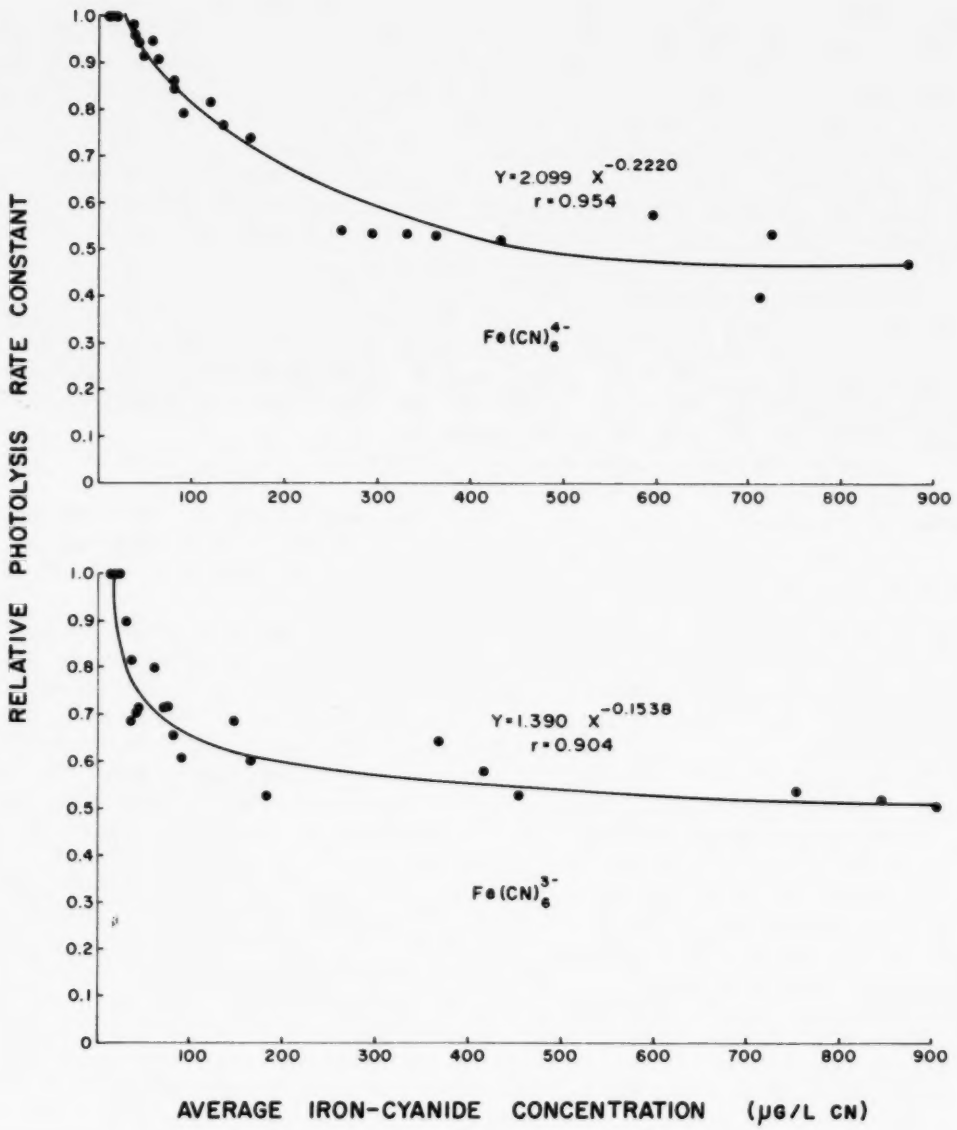

Figure 3. Relative photolysis rate constants normalized to the values determined for solutions with an initial total cyanide concentration of 25 µg/l CN and as a function of the average iron-cyanide concentration during the rate determination period.

for ferricyanide solutions is faster than for comparable ferrocyanide solutions.

The maximum amount of total cyanide that could be photochemically released as HCN from prolonged exposure of dilute hexacyanoferrate (II) and (III) solutions was determined to be about 85% and 49%, respectively. This indicates that for every mole of iron (II) and (III) complex, each containing 6 moles CN, only 5 and 3 moles of CN, respectively, can be released as free cyanide from the complex anions through a photolysis reaction. These results are not consistent with the reaction pathways for the photodecomposition of hexacyanoferrate complexes as proposed in the introduction (equations 1 and 4). This supports the contention of Balzani and Carassiti (1970) that the overall chemical changes and the reaction mechanisms for the photolysis of hexacyanoferrate complexes is not well defined.

Quantum Yield

Minimum direct photolysis rates of hexacyanoferrate (II) and (III) complex solutions prepared with deionized water were determined empirically at near-surface depths and midday for different times of the year under full sunlight at St. Paul, Minn. The experimental midday half-lives for hexacyanoferrate (II) solutions initially containing 100 µg/l CN at pH 7.8 and 20° C ranged from about 50 min in late fall to a minimum of about 18 min in midsummer (Figure 4). For comparable hexacyanoferrate (III) solutions the midday half-lives ranged from about 160 min in late fall to a minimum of about 64 min in midsummer (Figure 5).

The quantum yields (ϕ) for the photodecomposition of the iron-cyanide complexes were estimated by a visual best fit analysis of observed date-dependent midday half-lives, determined from the change in HCN concentration (eq. 8, p. 11), to the theoretical curves calculated for certain ϕ values and specific sunlight absorption rates (k_a) of the reactants as determined from the Zepp and Cline computer program. From our investigation it was experimentally determined that the iron-cyanide disappearance quantum yield as indicated by HCN formation for the hexacyanoferrate (II) and (III) complexes are approximately 0.14 and 0.0023, respectively (Figures 4 and 5). This calculation assumes that the quantum yields are wavelength independent in the region of sunlight absorption. Our experimentally determined quantum yields are in reasonable agreement with those reported in the review by Balzani and Carassiti (1970) (see p. 6).

Time of Year and Latitude

The intensity and spectral distribution of sunlight on a horizontal surface generally decreases with decreasing angular height of the sun. Therefore, intensity decreases from midday to sunset, from summer to winter, and from the tropics to higher latitudes. Midday half-lives for direct photolysis of hexacyanoferrate (II) and (III) complexes near the surface of an aqueous solution and as a function of time of the year and latitude are shown in Figure 6. The results were computed as relative values with the half-life of each complex on July 1 at latitude 45° N assigned a value of unity. For both complexes the photolysis half-lives at the midlatitudes are predicted to

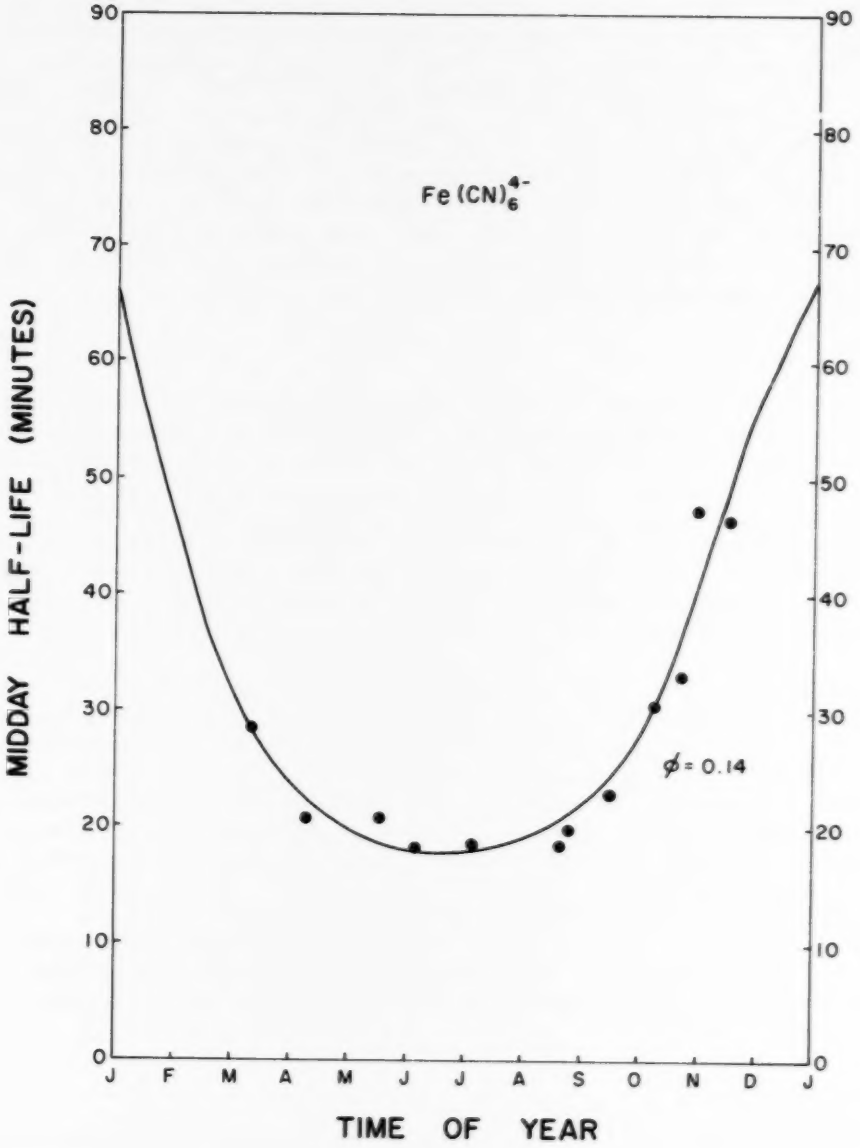

Figure 4. Midday half-lives for 100 µg/l CN hexacyanoferrate (II) solutions at near surface depths for different times of the year under full sunlight conditions at St. Paul, Minn.

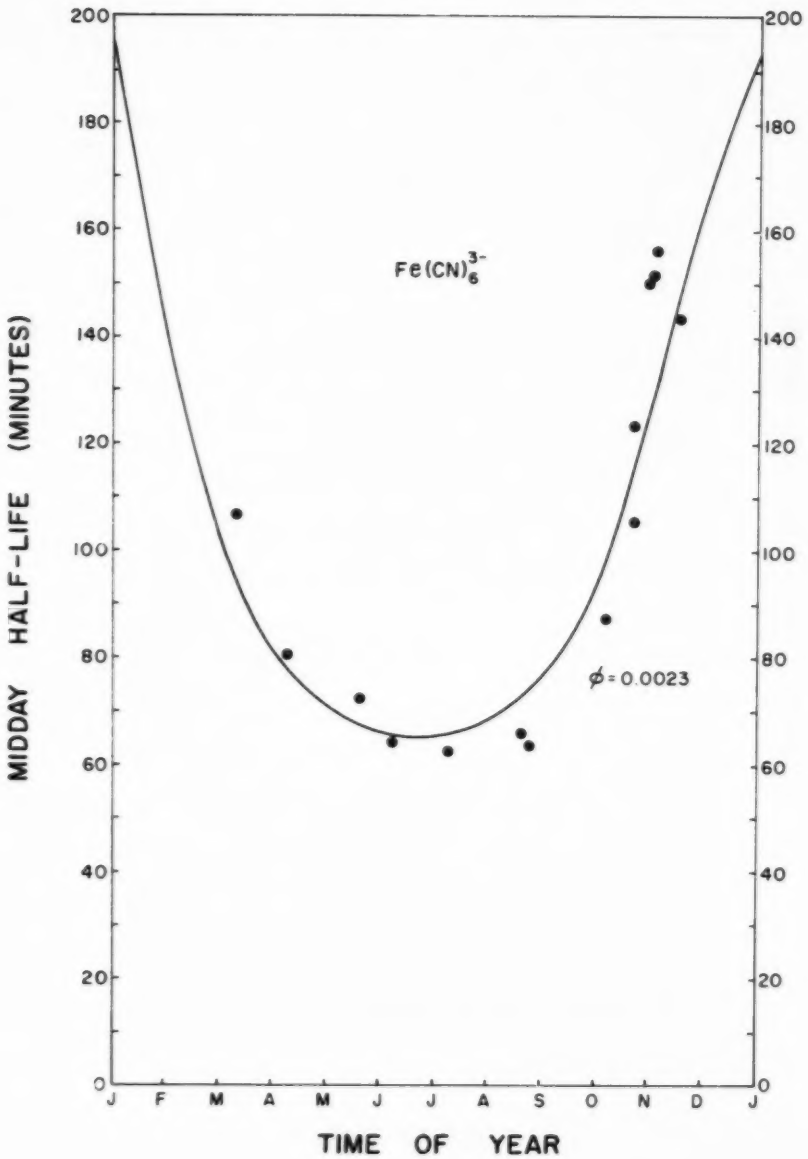

Figure 5. Midday half-lives for 100 µg/l CN hexacyanoferrate (III) solutions at near surface depths for different times of the year under full sunlight conditions at St. Paul, Minn.

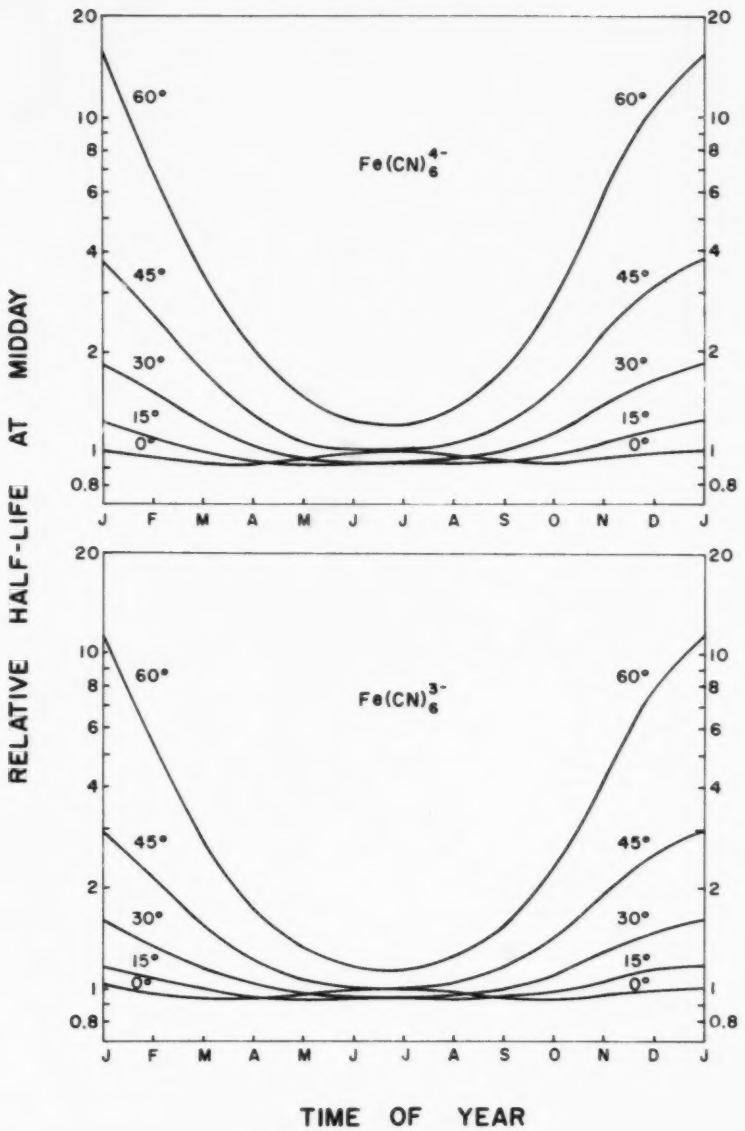

Figure 6. Midday half-lives for direct photolysis of pure water hexacyanoferrate (II) and (III) solutions (near surface) as a function of the time of year for several northern latitudes. Values are relative to July 1 rate at 45° N latitude.

be minimal during the summer and maximum during the winter months. Both the half-lives and the amplitude of the time of year variation increase with increasing northern latitude. In the tropical zone photolysis rates should be relatively constant throughout the year. Variations in rates during the summer are also expected to be minimal with less than a 1.3-fold increase from the equator to latitude 60° N. The relative half-lives for both iron-cyanide complexes are quite similar at all latitudes and times of the year. During the ice-free months, the variation in relative midday half-lives is expected to be less than a value of 3 on sunny days and for latitudes to 60° N.

Diurnal Change

The direct photolysis rate of iron-cyanide complexes changes diurnally as the intensity of sunlight increases and then decreases throughout the day, with maximum rates occurring at midday. This variation in computed rates for shallow depths and relative to photolysis rates at midday on July 1 at latitude 45° N, longitude 93.2° W is illustrated for the first of various months in Figures 7 and 8. Experimentally determined photolysis rates relative to midday values and as determined at different times of the day for pure water iron-cyanide solutions were close to the theoretically computed values as indicated in Figures 9 and 10.

Attenuation by Natural Waters

Light falling directly on the surface of a water body is both reflected at an angle equal to the angle of incidence and penetrates with a change in direction due to refraction. The fraction of direct sunlight and sky radiation that is reflected is small when compared with that which penetrates (Wetzel, 1975). The reflected light is essentially the same in spectral composition as incident light but the spectrum of light penetrating the surface of the water is altered. The intensity of incident collimated sunlight that penetrates natural waters, when compared with that of pure water, is attenuated through absorption and scattering. The reduction in transmission of light and shift in absorption selectivity depends on the wavelengths of the incident light and the depth to which the light has penetrated. In inland surface waters absorption is due mainly to dissolved metallic ions and natural organics. Attenuation coefficients (σ_λ) were measured for different water bodies with a Beckman DB-GT spectrophotometer and are presented in Appendix A. In all cases the attentuation of light was wavelength dependent and varied considerably from one water body to another (Figure 11). This is especially true for the ultraviolet region where attenuation of light intensity increases with decreasing wavelength.

Both suspended and dissolved materials within a water body induce variations in the depth of light penetration. Increasing turbidity decreases transparency and shifts maximum wavelength transmission to longer wavelengths. Substances in a solution that absorb or scatter light should diminish the photodecomposition rate of iron-cyanides by reducing the amount of light available. This effect was demonstrated by using turbid suspensions prepared with deionized water and bentonite colloidal clay or wind-blown silt from melted snow. The experiments were conducted with an apparatus consisting of a Pyrex glass filter containing 40 mm of the suspension and horizontally

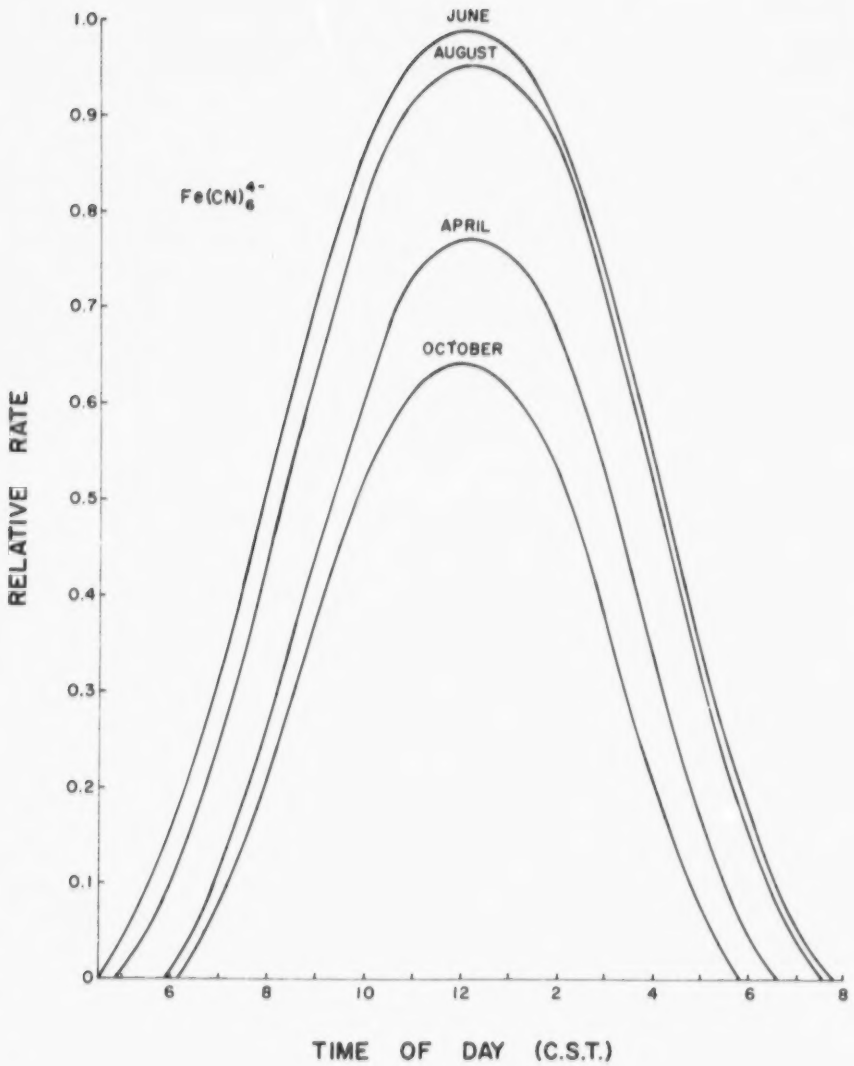

Figure 7. Diurnal variation of direct photolysis rates of pure water hexacyanoferrate (II) solutions (near surface) relative to photolysis rates at midday on July 1 at latitude 45° N, longitude 93.2° W.

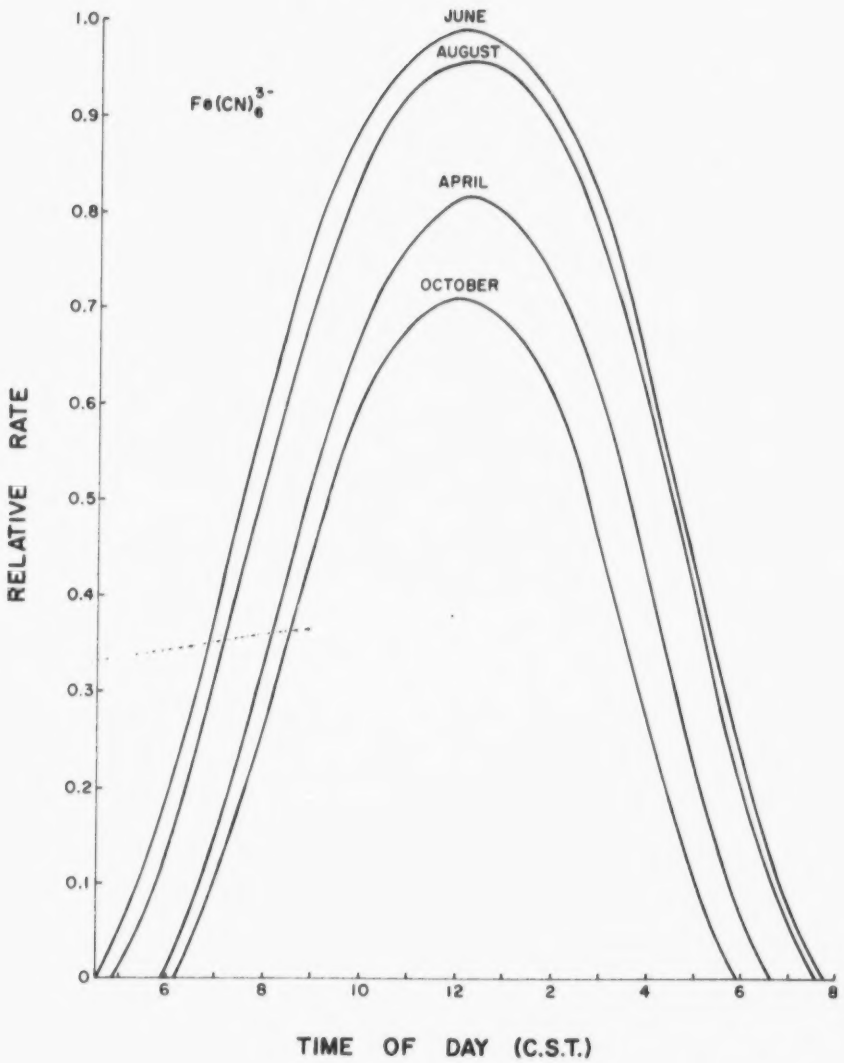

Figure 8. Diurnal variation of direct photolysis rates of pure water hexacyanoferrate (III) solutions (near surface) relative to photolysis rates at midday on July 1 at latitude 45° N, longitude 93.2° W.

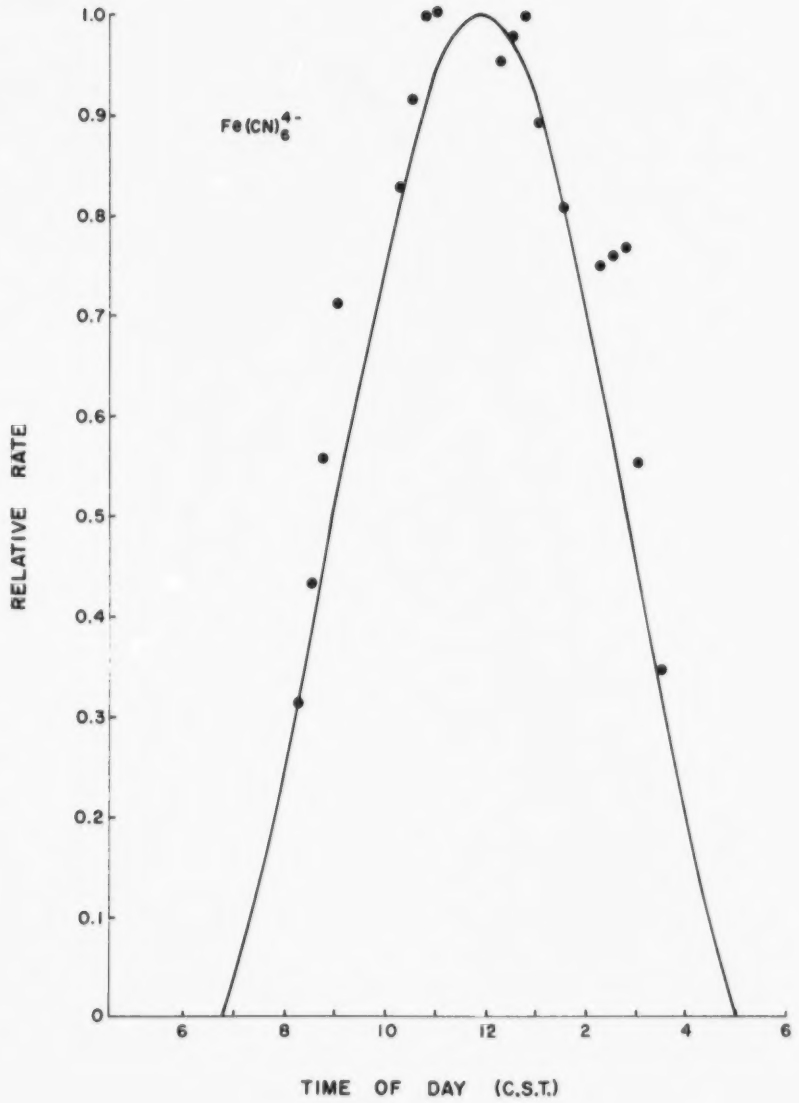

Figure 9. Time of day dependence of direct photolysis rates of pure water hexacyanoferrate (II) solutions (near surface) relative to photolysis rates for midday at St. Paul, Minn. on October 20, 1977. Theoretical relationship indicated by smooth line.

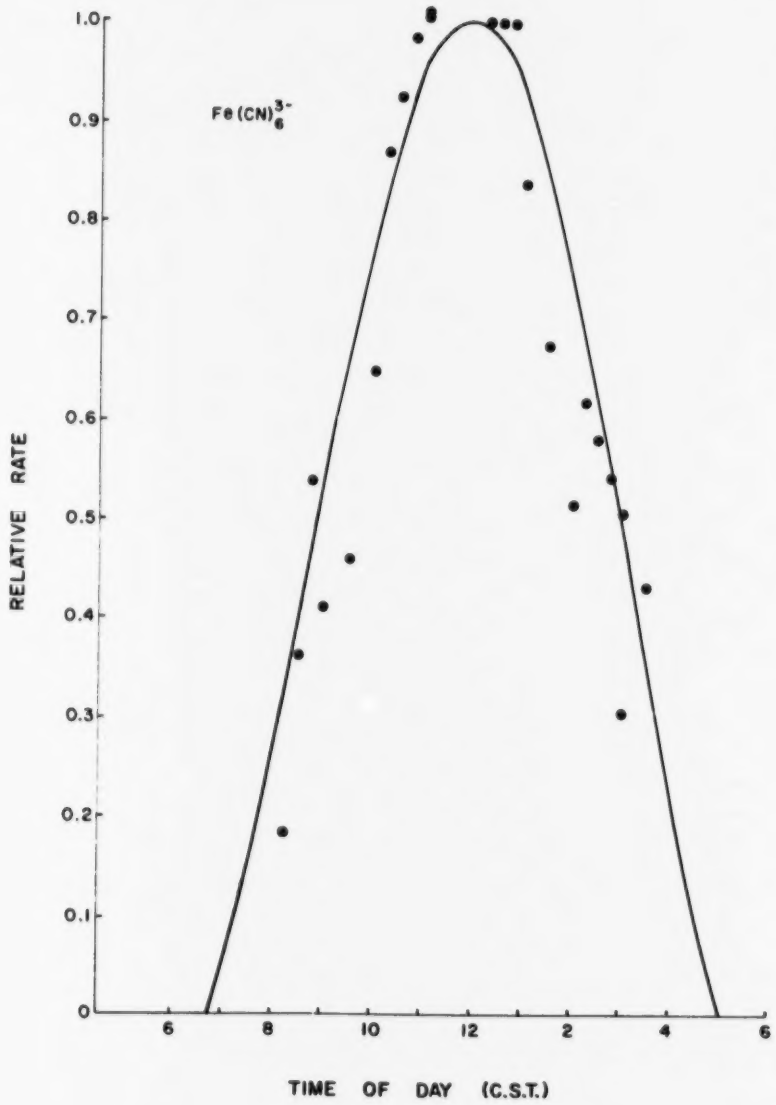

Figure 10. Time of day dependence of direct photolysis rates of pure water hexacyanoferrate (III) solutions (near surface) relative to photolysis rates for midday at St. Paul, Minn. on October 21, 1977. Theoretical relationship indicated by smooth line.

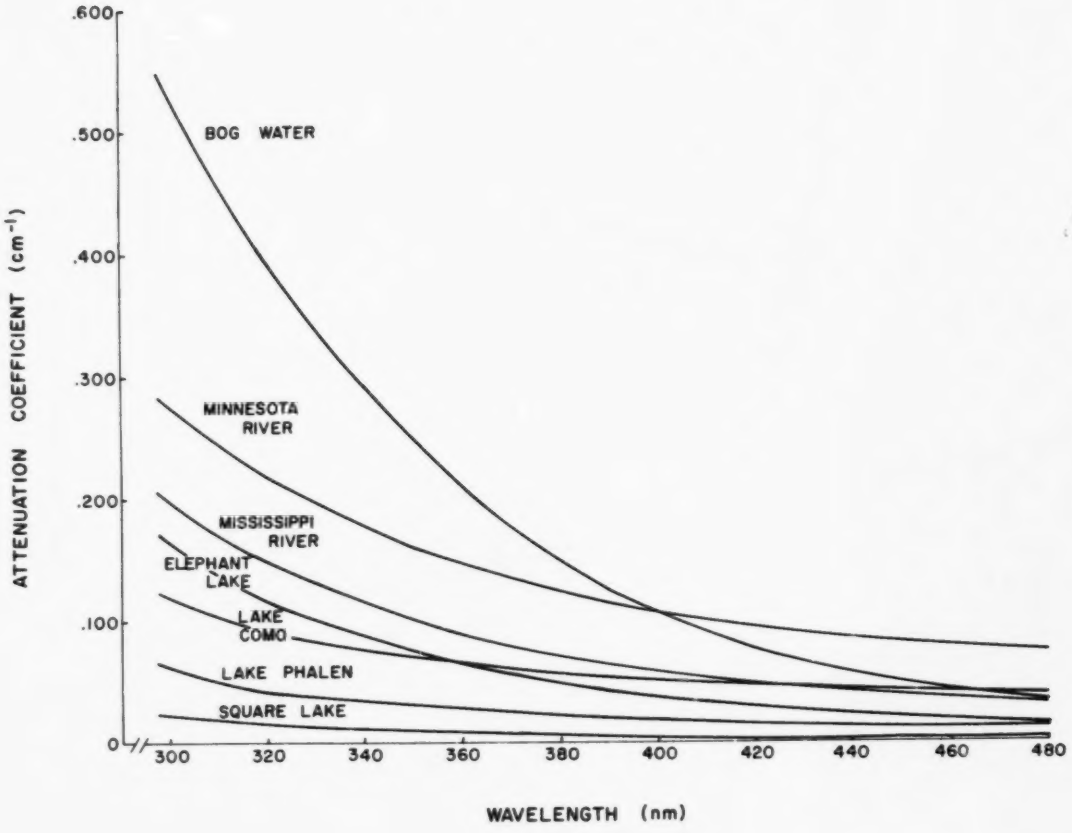

Figure 11. Attenuation coefficients relative to deionized water for natural water samples collected in north-central United States.

positioned over an open cylindrical jar which contained the iron-cyanide solutions at pH 7.8 and 20° C. In this manner, the suspensions were not in direct contact with the iron-cyanide solutions and all of the light reaching an iron-cyanide solution had to first pass through a filter. During the short exposure periods a negligible amount of suspended material settled out on the bottom of the filters.

Relative photolysis rates were defined as those normalized to rates determined for iron-cyanide solutions for which the overlying Pyrex filters contained 40 mm of deionized water. The ratios of the experimentally determined and theoretically computed relative photolysis rates of hexacyanoferrate (II) and (III) solutions as affected by suspensions of bentonite clay and wind-blown silt are presented in Table 5. The relationships between the ratios expressed as logarithms and turbidity were determined, as represented in Figure 12, to be linear at least to 40 NTU. These lines can be characterized for the bentonite solutions by a slope function (β) of 0.0618 and 0.0502 for the hexacyanoferrate (II) and (III) solutions, respectively. The slope for the relationship determined when light had to pass through wind-blown silt solutions before reaching hexacyanoferrate (II) solutions is 0.0456.

The total attenuation of radiance passing through a medium is due to absorption and to a redirection or scattering of some of the beams radiance. Determination of the forward scattering function requires artificial light which yields a collimated beam (Tyler and Preisendorfer, 1962). Therefore, this parameter could not be measured from our data. However, from Figure 12 it is apparent that the photolysis reaction in iron-cyanide solutions is enhanced by suspended materials when compared with that theoretically calculated from beam attenuation coefficients. In fact, one might expect up to a threefold to fourfold increase in photolysis rates when compared with those calculated for iron-cyanide solutions in natural waters with a turbidity of about 10 NTU. The photolysis reaction for ferrocyanide solutions is affected to a greater degree by the presence of bentonite than for ferricyanide solutions. The presence of wind-blown silt had less of an enhancement effect than that of bentonite on the photodecomposition of hexacyanoferrate (II) solutions (Figure 12). This may be due to a reduction in the forward scattering of light by silt solutions when compared with those prepared with bentonite.

The decrease in photolysis rate with increasing depth is dependent upon the relative magnitude of the attenuation coefficients of the water body, the molar extinction coefficients of the iron-cyanide complex, and the intensity of sunlight, all as a function of spectral wavelength. In general, the shorter wavelengths are more readily removed by the surface layer of most natural waters. Thus, the photochemically active light which decomposes iron-cyanides is expected to penetrate only a short distance in natural waters.

Field experiments on the photolysis of iron-cyanide solutions in natural waters were conducted by suspending test tubes containing cyanide solutions prepared with pH 7.8 phosphate buffered deionized water for a specific time period at known depths in a water column. Using beam attenuation coefficients and assuming photolysis at a specific depth, the depth-dependence of the

TABLE 5. EXPERIMENTALLY DETERMINED AND THEORETICALLY COMPUTED RELATIVE PHOTOLYSIS RATES FOR HEXACYANOFERRATE (II) AND (III) SOLUTIONS AS NORMALIZED TO DEIONIZED WATER CONTROLS AND AFFECTED BY BENTONITE AND WIND-BLOWN SILT. COMPUTED RATES ARE BASED ON BEAM ATTENUATION COEFFICIENT MEASUREMENTS

Test solution and concentration, (mg/l)		Turbidity, NTU	Relative photolysis rate normalized to controls		Ratio of A to B
			A Determined	B Computed	
			FERROCYANIDE		
Bentonite	75	6.7	0.916	0.365	2.51
Bentonite	250	24.0	0.632	0.0155	40.8
Bentonite	600	57.0	0.326	0.000147	2218
Bentonite	750	68.0	0.260	0.0000264	9848
Silt	-	23.0	0.403	0.0431	9.35
Silt	-	43.0	0.186	0.00197	94.4
Silt	-	63.0	0.0824	0.000107	770.1
			FERRICYANIDE		
Bentonite	75	5.6	0.958	0.471	2.03
Bentonite	100	9.9	0.960	0.240	4.00
Bentonite	200	18.5	0.805	0.0906	8.88
Bentonite	250	23.0	0.872	0.0405	21.5
Bentonite	400	36.4	0.528	0.00936	56.4
Bentonite	500	46.0	0.603	0.00244	247.1
Bentonite	600	54.0	0.421	0.00111	379.3

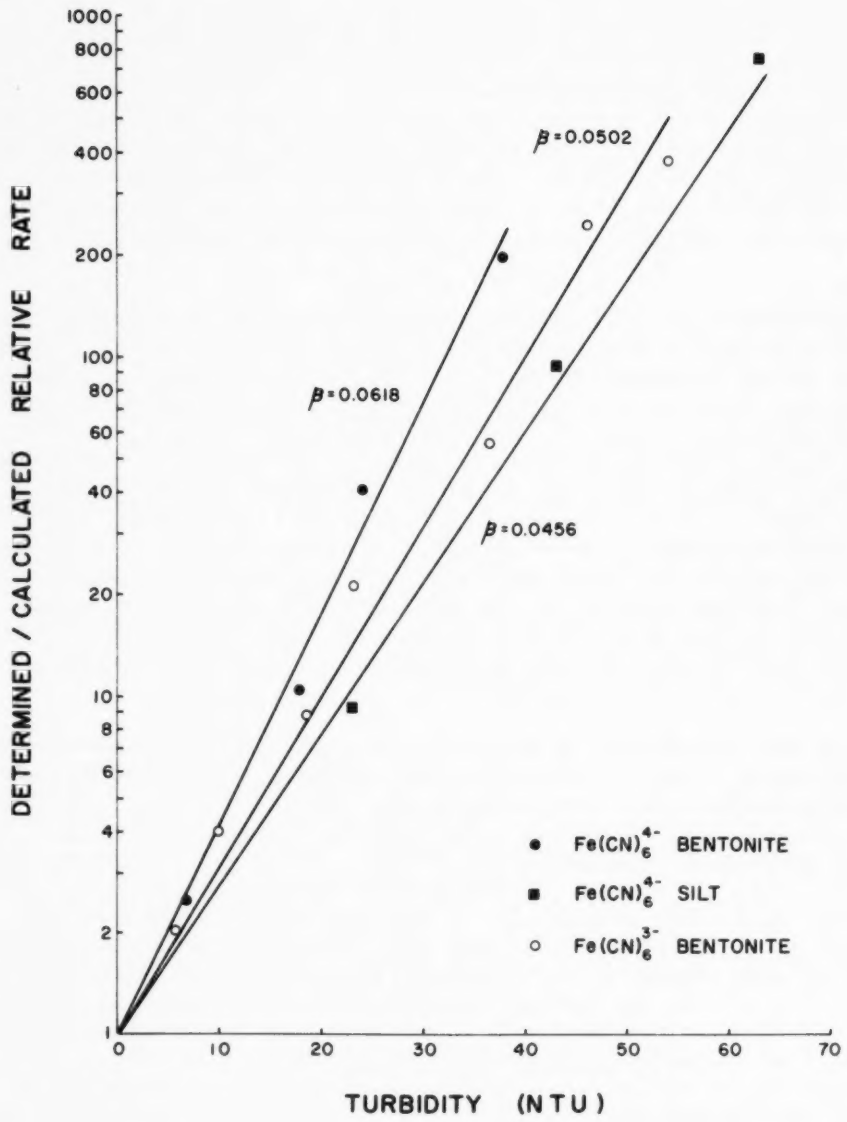

Figure 12. Influence of turbidity on the experimentally determined to theoretically calculated relative photolysis rate of hexacyanoferrate (II) and (III) solutions.

direct photolysis of hexacyanoferrate (II) and (III) solutions relative to near-surface rates were computed with the Zepp and Cline (1977) computer program for latitude 45° N, longitude 93.2° W. The photolysis rates normalized to that at the surface decreased exponentially with depth. The linear regression lines defining these relationships were calculated by forcing the line through the log relative rate of 1.0 at depth 0 cm. The theoretical and determined rates of decrease in the depth-dependent photolysis of hexacyanoferrate (II) and (III) solutions are presented in Table 6. The regression lines apply to relative photolysis rates as low as one-hundredth of that determined at the surface. The photolysis rate for hexacyanoferrate (II) solutions decreases more rapidly with increasing depth than the rate for hexacyanoferrate (III) solutions. The rates differ because the predominant wavelengths affecting photolysis of the iron (II) complex are shorter and thus penetrate less into natural waters than those activating the iron (III) complex.

The ratio of the theoretical to determined rate of decrease in photolysis rates varied from near 1.0 for Square Lake and bog waters of low turbidity to 3.52 for the turbid Minnesota River. The ratios are apparently a function of turbidity or suspended solids, since for Square Lake and bog water the observed and theoretical rates of decrease were almost identical. The theoretical computations assume that the natural materials in a water body act only as photochemically inert sun screens. Reactions by "sensitizers" and the bouncing of light or light scattering in turbid solutions which may increase photolysis over that predicted is ignored. However, it was observed that in the more turbid waters the photolysis reaction was relatively enhanced with depth because of light scattering and thus the rate of decrease in photolysis rate with depth is less than theoretically predicted by the Zepp and Cline model. These results confirm the relationship between turbidity and photolysis rate as presented in Figure 12.

By using the attenuation coefficients in Appendix A and assuming complete mixing of the water column of interest, the depth-dependence of the average direct photolysis rates for hexacyanoferrate (II) solutions at midday and midsummer relative to near-surface rates were calculated for latitude 40° N by the computer program of Zepp and Cline (1977). These relationships are shown in Figure 13. From the results in Table 6 for photolysis rates at a point for various depths in a water column, it is proposed that the theoretical relationships actually overestimate the rate at which the relative photolysis rate decreases when mixing is assumed. For waters like the Minnesota River, the rate of decrease may in fact be overestimated by a factor of about 3.5 (Table 6). For the natural waters tested the average observed decrease is about one-half as rapid as that theoretically predicted in Figure 13. If this factor is applied to the computed depth-dependence curves where mixing of the water column was assumed (Figure 13), it is proposed that below a depth of about 50 - 100 cm photolysis of hexacyanoferrate (II) is insignificant from a toxicological standpoint in all tested natural waters. A relationship for the hexacyanoferrate (III) complex was not included since the concentration of HCN formed by photolysis of this complex in solutions prepared with natural waters was approximately the same as that produced in comparable hexacyanoferrate (II) solutions.

TABLE 6. PHYSICAL PROPERTIES OF VARIOUS NATURAL WATERS AND THE THEORETICAL AND DETERMINED RATE OF DECREASE IN THE DEPTH-DEPENDENT DIRECT PHOTOLYSIS RATE OF HEXACYANOFERRATE (II) AND (III) SOLUTIONS PREPARED WITH DEIONIZED WATER AND EXPOSED TO NATURAL LIGHT AT SPECIFIC FIXED DEPTHS AT LATITUDE 45° N, LONGITUDE 93.2° W

Water body	Secchi disk measurement, cm	Turbidity, NTU	Residue, mg/l			Linear regression slope values*			Ratio of A to B
			Total filterable	Total non filterable	Total	A theoretical	B determined	R^2	
				FERROCYANIDE					
Square Lake	-	0.43	-	-	-	-0.0118	-0.0107	0.984	1.10
Lake Phalen	202	2.7	223	3.0	226	-0.0364	-0.0190	0.990	1.92
Lake Como	79	5.4	190.5	11.0	201.5	-0.0884	-0.0392	0.998	2.26
Elephant Lake	180	2.9	74	<1	74	-0.0886	-0.0453	0.927	1.96
Mississippi River	-	3.6	-	-	-	-0.130	-0.0850	0.947	1.53
Minnesota River	45	14.0	495	24.5	519.5	-0.206	-0.0586	0.939	3.52
Bog water	-	0.9	-	-	-	-0.290	-0.260	0.978	1.12
				FERRICYANIDE					
Square Lake	-	0.43	-	-	-	-0.00516	-0.00482	0.956	1.07
Lake Phalen	202	2.7	223	3.0	226	-0.0201	-0.00956	0.925	2.10
Lake Como	79	5.4	190.5	11.0	201.5	-0.0590	-0.0314	0.998	1.88
Elephant Lake	180	2.9	74	<1	74	-0.0338	-0.0226	0.972	1.50
Mississippi River	-	3.6	-	-	-	-0.0939	-0.0461	0.976	2.04
Minnesota River	45	14.0	495	24.5	519.5	-0.121	-0.0444	0.996	2.73
Bog water	-	0.9	-	-	-	-0.112	-0.120	0.982	0.93

*Linear regression analysis for log relative photolysis rates (Y) normalized to those determined for comparable solutions at the surface and depth (X) in cm. Regression lines are forced through the log relative photolysis rate of 1.0 at depth of 0 cm. Log $Y = \beta X$ with $\beta = \frac{\Sigma XY}{\Sigma X^2}$ (Steel and Torrie, p. 179, 1960).

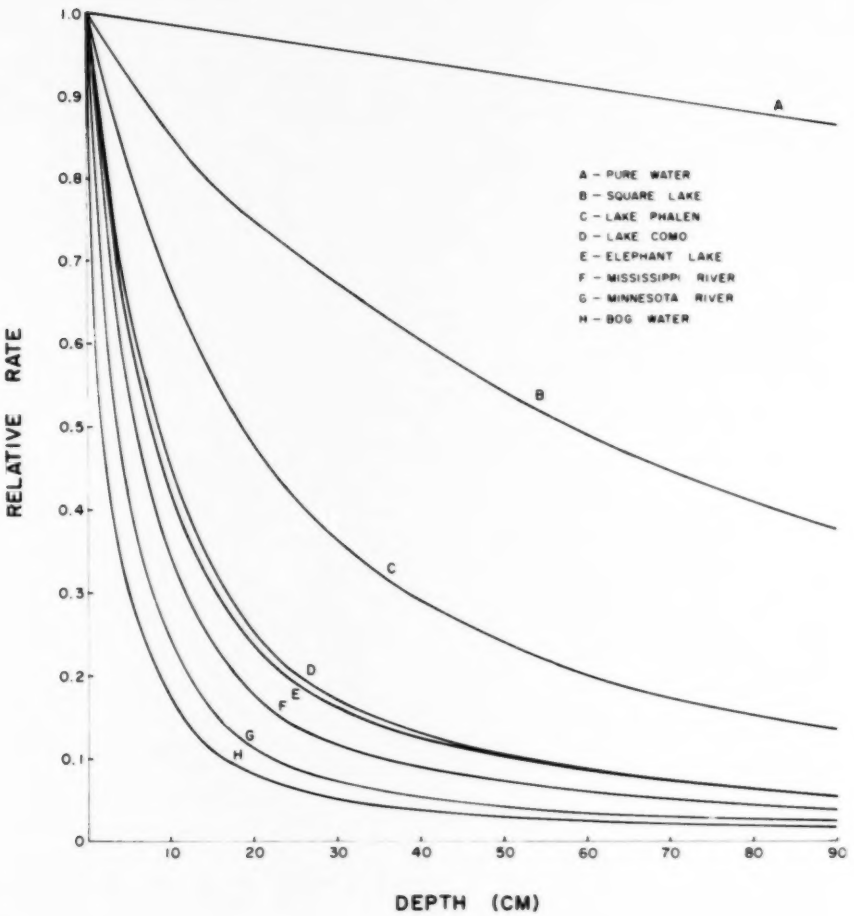

Figure 13. Calculated depth-dependence of the direct photolysis of hexacyanoferrate (II) at midday and midsummer for latitude 40° N when using beam attenuation coefficients and assuming complete mixing of the water column.

In making the depth-dependent computations, it was assumed that the iron-cyanide is isotropically distributed and all that is in a water layer is exposed to the same amount of light during a given time period. This assumption has been demonstrated according to Zepp and Cline (1977) to be valid at depths in which a small fraction of the incident light is absorbed. However, if at a given depth almost all of the light is absorbed in the upper part of the water column, the assumptions are valid only if mixing is more rapid than entry of iron-cyanide into or loss from the upper layer of the water body. If entry to the upper layer is more rapid than mixing, then the concentration of iron-cyanide and thus HCN will be higher than predicted near the surface. If a situation exists in which the iron-cyanide is initially uniformly distributed in the water column but mixing is incomplete, then it would be expected that the photolysis rate would be slower with increasing depth than is indicated in Figure 13. The above calculations apply to near midday and summer situations. As the sun moves lower in the sky as a function of the time of day or latitude, the underwater path length of direct sunlight is longer and depth dependence increases.

Sky Conditions and Photolysis Rate

The daytime radiation received at any point on the earth's surface consists of direct solar radiation or sunlight, and indirect solar radiation or scattered light of the sky. The spectral distribution of irradiance reaching the earth's surface depends on the sun's altitude and the meteorological conditions of the intervening atmosphere. The relative spectral composition of the energy distribution of combining solar and sky radiation between 315 and 800 nm is essentially constant during the day (Robinson, 1966). However, a reduction in atmospheric clarity contributes to a decrease in intensity of light falling on the surface of a water body. Measurements of the relative spectral distribution of the radiation which penetrates a cloud or an overcast indicate that it will be essentially the same as that which enters (Hull, 1954, and Leighton, 1961). Therefore, the relative energy/wavelength curve of sun and sky radiation together is nearly the same on a clear and overcast day. This phenomenon was tested by determining the photolysis rate as a function of solar radiation, both normalized to that predicted by interpolation from results for clear days. This relationship is depicted in Figure 14. Since the experimentally determined observations are close to the 45° line in Figure 14, it can be concluded that the photodecomposition of hexacyanoferrate (II) and (III) solutions is a direct function of natural light intensity for various meteorological conditions.

Photolysis in Natural Waters

The rate of photodecomposition at 15° C for hexacyanoferrate (II) solutions initially containing 100 µg/l CN and in Pyrex test tube cells exposed to natural light was essentially the same when different waters were used in preparation of the test solutions. This is demonstrated in Table 7 by the similarity in photolysis rates for solutions prepared with different unfilterd natural waters relative to the rates determined for comparable solutions prepared with deionized water. The slight reduction (Table 7) in relative photolysis rate for solutions prepared with Minnesota or Mississippi

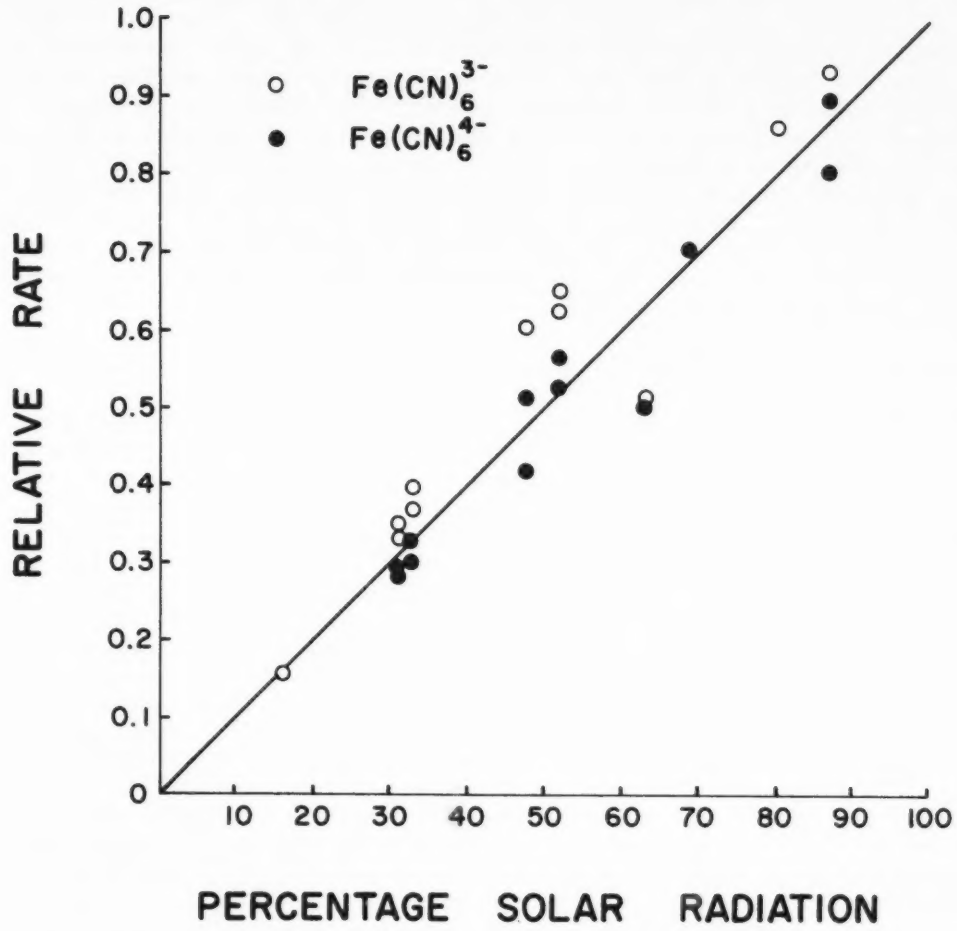

Figure 14. Relationship between photolysis rate and solar radiation, both normalized to that predicted for a clear day.

TABLE 7. DETERMINED PHOTOLYSIS RATES FOR HEXACYANOFERRATE (II) SOLUTIONS PREPARED WITH DIFFERENT WATERS RELATIVE TO THE RATES FOR SIMILARLY EXPOSED SOLUTIONS PREPARED WITH DEIONIZED WATER

Type of water	Test pH	Relative photolysis rate
Deionized	7.9	1.000
Well	8.1	1.044
Lake Phalen	7.6	0.988
Lake Como	8.5	1.096
Elephant Lake	7.4	0.991
Mississippi River	8.5	0.819
Minnesota River	7.5	0.960

River water is probably due to the decreased light penetration into the 2 cm path length of the cells containing natural water solutions relative to those prepared with deionized water. Therefore, the relationships presented in previous sections, as determined for deionized water solutions, are appropriate for hexacyanoferrate (II) solutions prepared with several different natural waters.

Various natural waters and chemicals were used to determine empirically the effect of materials in different waters on the photolysis rate of $Fe(CN)_6^{3-}$. These results are summarized in Table 8 where the photolysis rate at 15° C of hexacyanoferrate (III) solutions initially containing 100 µg/l CN and prepared with various waters are compared to the rates determined for similarly exposed solutions prepared with deionized water. The Fe^{++} ion from the addition of ferrous chloride under near-zero dissolved oxygen levels enhanced the photolysis rate, whereas Fe^{+++} ion added as ferric chloride or that derived from the oxidation of Fe^{++} depressed the reaction. The presence of ammonia (ammonium chloride) and nitrate (sodium nitrate) had no effect on the photolysis rate, but dissolved sulfide (sodium sulfide) dramatically enhanced the photodecomposition reaction. The photolysis rates for ferricyanide solutions prepared with several different natural surface waters and well water were about twice as great in the natural water as in deionized water (Table 8). This acceleration may be attributed to the rapid reduction of hexacyanoferrate (III) to the more photochemically active hexacyanoferrate (II). This possibility is supported by the fact that the ratios of photolysis rates at 15° C for comparable ferri- and ferrocyanide solutions initially containing 100 µg/l CN and prepared with the same natural surface water from various sources averaged 0.92 (Table 9). If our results for experiments conducted with natural waters are typical of other waters, then it is believed that iron-cyanides in effluents being discharged into various natural waters will photochemically respond like hexacyanoferrate (II) ions, since essentially no $Fe(CN)_6^{3-}$ ions will be present in the receiving waters.

This study has demonstrated a means by which the cyanide in relatively nontoxic iron-cyanide complexes may, under certain conditions, be largely liberated as toxic free cyanide in natural waters. The rate of this process and the concentration of free cyanide produced can be approximately predicted from information derived in our study and by utilizing the computer program of Zepp and Cline (1977). These calculations can be made as a function of longitude, latitude, time of day and year, and depth in a natural water body. The extent of the photolysis reaction will be a function of the iron-cyanide concentration and the degree and duration of illumination. Photolysis may be negligible in deep, turbid, or shaded waters, and the slowly liberated nonpersistent free cyanide may decrease or escape as rapidly as it is released. However, in relatively clear shallow waters, or in situations where effluents are stratified in the light penetration zone, the photodecomposition of iron-cyanides may produce free cyanide concentrations in the µg/l range that could adversely affect the distribution and abundance of aquatic organisms (Smith et al., 1979).

TABLE 8. DETERMINED PHOTOLYSIS RATES FOR HEXACYANOFERRATE (III) SOLUTIONS PREPARED WITH DIFFERENT WATERS RELATIVE TO THE RATES FOR SIMILARLY EXPOSED SOLUTIONS PREPARED WITH DEIONIZED WATER (DW)

Type of water[a]	Test pH	Relative photolysis rate
Deionized	7.8	1.000
DW + 0.5 mg/l Fe^{+++} (DO)	6.2	0.790
DW + 0.5 mg/l Fe^{++} (DO)	6.6	1.486 → 0.450[b]
DW + 0.5 mg/l Fe^{++} (near zero DO)	7.3	2.995 → 1.690[b]
DW + 5.0 mg/l Fe^{++} (DO)	6.0	approx. 0
DW + 0.5 mg/l NH_4^+ (DO)	7.5	1.095
DW + 0.5 mg/l NO_3^- (near zero DO)	7.2	0.970
DW + 0.5 mg/l sulfide (near zero DO)	7.6	2.309
WW - after Fe removal[c] (DO)	7.6	1.370
WW - after Fe removal[c] (near zero DO)	8.7	1.692
WW - before Fe removal[c] (DO)	8.4	2.228
Elephant Lake	7.3	2.299
Lake Como	8.5	2.157
Minnesota River	7.7	1.988
Mississippi River	8.3	1.758
Bog	7.2	1.528[d]

[a]DO refers to solutions that were aerated prior to exposure and it is assumed that dissolved oxygen concentrations were near saturation

Near zero DO refers to solutions that were stripped with N_2 prior to exposure and it is assumed that dissolved oxygen concentrations were near zero.

[b]Rate decreased during exposure period.

[c]Removal of iron from the well water (WW) was accomplished by a Culligan catalytic system which converts Fe(II) to Fe(III). Iron concentrations were approximately 0.3 mg/l before and <0.05 mg/l after removal.

[d]Low because of strong light absorption (Figure 11) by bog water relative to deionized water solutions in test tube exposure cells.

TABLE 9. RATIO OF DETERMINED PHOTOLYSIS RATES FOR HEXACYANOFERRATE (III) TO (II) SOLUTIONS OF EQUAL INITIAL TOTAL CYANIDE CONCENTRATION PREPARED WITH DIFFERENT WATER TYPES AND EXPOSED TO THE SAME NATURAL LICHT CONDITIONS

Type of water	Ratio of photolysis rates
Deionized	0.417
WW - after Fe removal	0.694
WW - before Fe removal	1.090
Lake Como	0.869
Elephant Lake	0.921
Mississippi River	0.938
Minnesota River	0.868
Bog	0.987

REFERENCES

Adamson, W. 1952. Electron Transfer Processes and the Oxidation-Reduction Reactions of Hexacyanoferrate (III) Ion in Aqueous Solution. J. Phys. Chem. 56: 858-862.

Alich, Sister M. A., D. T. Haworth, and Sister M. F. Johnson. 1967. Spectrophotometric Studies of Hexacyanoferrate (III) ion and its Reaction with Iron (III) in Water and Ethanol. J. Inorg. Nucl. Chem. 29(7): 1637-1642.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1971. Standard Methods for the Examination of Water and Wastewater. 13th ed. Washington, D.C. 874 p.

Asperger, S. 1952. Kinetics of the Decomposition of Potassium Ferrocyanide in Ultra-Violet Light. Trans. Faraday Soc. 48: 617-624.

Asperger, S., I. Murati, and D. Pavlovic. 1960. Kinetics and Mechanism of the Decomposition of Complex Cyanides of Iron (II) and Molybdenum (IV). J. Chem. Soc. 730-736.

Balzani, V., and V. Carassiti. 1970. Photochemistry of Coordination Compounds. Academic Press, New York, N.Y. 432 p.

Bener, P. 1972. Approximate Values of Intensity of Natural Ultraviolet Radiation for Different Amounts of Atmospheric Ozone. U.S. Army Report DAJA 37-68-C-1017, Davos Platz, Switzerland.

Broderius, S. J. 1973. Determination of Molecular Hydrocyanic Acid in Water and Studies of the Chemistry and Toxicity to Fish of Metal-Cyanide Complexes. Ph.D. Thesis. Oregon State University, Corvallis, Oregon. 287 p.

Broderius, S. J., and L. L. Smith, Jr. 1977. Direct Determination and Calculation of Aqueous Hydrogen Sulfide. Anal. Chem. 49: 424-428.

Broderius, S. J., and L. L. Smith, Jr. 1979. Lethal and Sublethal Effects of Binary Mixtures of Cyanide and Hexavalent Chromium, Zinc, or Ammonia to the Fathead Minnow (Pimephales promelas) and Rainbow Trout (Salmo gairdneri). J. Fish. Res. Board Can. 36: 164-172.

Broderius, S. J., L. L. Smith, Jr., and D. T. Lind. 1977. Relative Toxicity of Free Cyanide and Dissolved Sulfide Forms to the Fathead Minnow (Pimephales promelas). J. Fish. Res. Board Can. 34: 2323-2332.

Burdick, G. E., and M. Lipschuetz. 1950. Toxicity of Ferro- and Ferricyanide Solutions to Fish, and Determination of the Cause of Mortality. Trans. Am. Fish. Soc. 78: 192-202.

Carassiti, V., and V. Balzani. 1960. Photochemistry of Complex Salts in Solution: IV. Kinetics of the Photochemical and Thermal Decomposition of Potassium Ferrocyanide. Annali Di Chimica (Rome). 50: 782-789.

Doudoroff, P. 1976. Toxicity to Fish of Cyanides and Related Compounds. A Review. EPA-600/3-76-033, U.S. Environmental Protection Agency, Duluth, Minn. 155 p.

Emschwiller, G., and J. Legros. 1954. The Photolysis of Potassium Ferrocyanide in Aqueous Solution. Comptes Rendus. 239: 1491-1493.

Hull, J. N. 1954. Spectral Distribution of Radiation from Sun and Sky. Trans. Illum. Eng. Soc. (London). 19: 21-28.

Hutchinson, G. E. 1957. A Treatise on Limnology Vol. I - Geography, Physics, and Chemistry. Wiley and Sons, New York, N.Y. 1015 p.

Ibers, J. A., and N. Davidson. 1951. On the Interaction Between Hexacyanatoferrate (III) Ions and (a) Hexacyanatoferrate (II) or (b) Iron (III) Ions. J. A. Chem. Soc. 73: 476-478.

Kobayashi, T., and K. Mori. 1973. Formation of Compounds Toxic to Fish from Ferro- and Ferricyanides by Photodecomposition (Occurrence of Toxicity to Fish by Photodecomposition of Complex Cyanides). Nihon Mizu Shori Gijutsu Kenkyuhai, Mizu. Shori. Gijutsu. 14(6): 575-579.

Kongiel-Chablo, I. 1966. Behavior of Complex Cyanides in Natural Water with High Rate of Contamination. Roczniki Panstwowego Zakladu Hig. 17(1): 95-102.

Leighton, P. A. 1961. Photochemistry of Air Pollution. Academic Press, New York, N.Y. 300 p.

London, J. 1963. The Distribution of Total Ozone in the Northern Hemisphere. Beitr. Phys. Atmos. 36: 254-263.

Lure, Y. Y., and V. A. Panova. 1964. Behavior of Cyanide Compounds in Water Ponds. Gidrokhim Materialy. 37: 133-143.

MacDiarmid, A. G., and N. F. Hall. 1953. Illumination - pH Effects in Solutions of Complex Cyanides. J. Am. Chem. Soc. 75: 5204-5207.

Mitra, R. P., D. V. S. Jain, A. K. Bannerjee, and K. V. Raghavachari. 1963. Role of Free Radicals in the Photo-Oxidation of Fe^{+2} in Acidic Solutions of Ferrocyanide. Nature. 200: 163-164.

Moggi, L., F. Bolletta, V. Balzani, and F. Scandola. 1966. Photochemistry of Coordination Compounds-XV Cyanide Complexes. J. Inorg. Nuclear Chem. 28: 2589-2597.

Myers, C. S., and T. Iezzi. 1950. A Report of Experiments on the Effects of Certain Toxicants on Fish Life with Especial Reference to the Effects of Photodecomposition. Ind. Wastes Division, Bureau of San. Engr., Penn. Dept. of Health, Harrisburg, Penn. 10 p.

Ohno, S. 1967. The Photochemistry of Aqueous Hexacyanoferrate (II) Solutions. I. Photo-Aquation Reaction at 3660 Å. Bull. Chem. Soc. Japan. 40: 1765-1769.

Ohno, S., and G. Tsuchihashi. 1965. The Photochemistry of Hexacyanoferrate (II) Ions in Aqueous Solutions. Bull. Chem. Soc. Japan. 38(6): 1052-1053.

Palaty, J., and M. Horokova-Jakubu. 1959. The Course and Rate of Removal of Cyanides from Water Under Natural Conditions. Sbornik Vscht, Prague, Oddil Fak. Tech. Paliv A Vody. 3(1): 83-110.

Robinson, N. 1966. Solar Radiation. Elsevier Publishing Company, New York, N.Y. 347 p.

Smith, L. L., Jr., S. J. Broderius, D. M. Oseid, G. L. Kimball, W. M. Koenst, and D. T. Lind. 1979. Acute and Chronic Toxicity of HCN to Fish and Invertebrates. EPA-600/3-79-009, U.S. Environ. Prot. Agency, Duluth, Minn. 115 p.

Steel, R. G. D., and J. H. Torrie. 1960. Principles and Procedures of Statistics with Special Reference to the Biological Sciences. McGraw-Hill Book Co., Inc. New York, N.Y. 481 p.

Stumm, W., and J. J. Morgan. 1970. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley and Sons, Inc., New York, N.Y. 583 p.

Terhaar, C. J., W. S. Ewell, S. P. Dziuba, and D. W. Fassett. 1972. Toxicity of Photographic Processing Chemicals to Fish. Photogr. Sci. Eng. 16: 370-377.

Tyler, J. E., and R. W. Preisendorfer. 1962. Transmission of Energy Within the Sea. In: The Sea, Vol. I, M. H. Hill, ed. Interscience, New York, N.Y., pp. 397-451.

West, L. E. 1970. Disposal of Waste Effluents from Motion-Picture Film Processing. J. Soc. Motion Picture Tel. Eng. 79: 765-771.

Wetzel, R. G. 1975. Limnology. W. B. Sanders Co., Philadelphia, Penn. 743 p.

Zepp, R. G., and D. M. Cline. 1977. Rates of Direct Photolysis in Aquatic Environment. Environ. Sci. Technol. 11(4): 359-366.

APPENDIX A
BEAM ATTENUATION COEFFICIENTS

Water body Turbidity (NTU)	Deionized	Bentonite Solutions								
	-	5.6	6.7	9.9	23.0	24.0	46.0	54.0	57.0	68.0
Wave length (nm)										
297.5	0.0028	0.118	0.122	0.221	0.509	0.527	0.963	1.081	1.131	1.387
300.0	0.0028	0.114	0.121	0.216	0.496	0.516	0.951	1.060	1.102	1.367
302.5	0.0026	0.113	0.119	0.213	0.487	0.509	0.924	1.041	1.086	1.328
305.0	0.0025	0.110	0.116	0.208	0.478	0.498	0.910	1.018	1.066	1.310
307.5	0.0024	0.108	0.114	0.203	0.469	0.491	0.893	1.004	1.046	1.292
310.0	0.0023	0.107	0.112	0.201	0.462	0.481	0.879	0.991	1.032	1.276
312.5	0.0022	0.105	0.110	0.199	0.455	0.475	0.866	0.971	1.009	1.252
315.0	0.0021	0.103	0.109	0.195	0.450	0.469	0.857	0.963	1.000	1.237
317.5	0.0020	0.102	0.108	0.192	0.444	0.463	0.848	0.951	0.991	1.222
320.0	0.0019	0.101	0.107	0.189	0.438	0.457	0.833	0.939	0.983	1.208
323.1	0.0018	0.099	0.106	0.187	0.429	0.450	0.824	0.924	0.963	1.187
330.0	0.00152	0.096	0.102	0.181	0.419	0.438	0.799	0.900	0.943	1.155
340.0	0.00122	0.093	0.098	0.174	0.399	0.420	0.770	0.866	0.907	1.114
350.0	0.00100	0.090	0.096	0.169	0.387	0.405	0.745	0.839	0.876	1.081
360.0	0.00082	0.088	0.095	0.166	0.377	0.391	0.721	0.815	0.848	1.046
370.0	0.00069	0.085	0.092	0.160	0.365	0.377	0.697	0.788	0.818	1.013
380.0	0.00056	0.082	0.089	0.154	0.351	0.364	0.674	0.759	0.790	0.979
390.0	0.00043	0.079	0.086	0.149	0.339	0.349	0.652	0.735	0.764	0.947
400.0	0.00035	0.076	0.082	0.143	0.328	0.337	0.631	0.710	0.742	0.914
410.0	0.00030	0.072	0.080	0.138	0.317	0.327	0.609	0.690	0.719	0.886
420.0	0.00026	0.070	0.076	0.134	0.308	0.316	0.590	0.672	0.699	0.857
430.0	0.00023	0.067	0.073	0.130	0.299	0.305	0.575	0.654	0.678	0.836
440.0	0.00020	0.065	0.070	0.125	0.291	0.294	0.559	0.635	0.660	0.815
450.0	0.00017	0.061	0.068	0.121	0.281	0.286	0.545	0.618	0.642	0.790
460.0	0.00016	0.060	0.066	0.118	0.274	0.277	0.535	0.604	0.629	0.772
470.0	0.00016	0.057	0.064	0.114	0.268	0.269	0.521	0.590	0.618	0.750
480.0	0.00016	0.056	0.061	0.112	0.260	0.263	0.509	0.577	0.602	0.735

APPENDIX A
BEAM ATTENUATION COEFFICIENTS

Water body	Wind-blown silt			Square Lake	Lake Phalen	Lake Como	Elephant Lake	Mississippi River	Minnesota River	Bog Water
Turbidity (NTU)	23.0	43.0	63.0	0.43	2.7	5.4	2.9	3.6	14.0	0.9
Wave length (nm)										
297.5	0.346	0.688	1.022	0.023	0.066	0.123	0.171	0.206	0.283	0.548
300.0	0.343	0.680	1.000	0.022	0.061	0.119	0.164	0.197	0.275	0.527
302.5	0.338	0.674	0.996	0.021	0.059	0.114	0.156	0.190	0.268	0.509
305.0	0.334	0.664	0.991	0.020	0.056	0.109	0.149	0.182	0.260	0.491
307.5	0.330	0.658	0.971	0.018	0.052	0.107	0.143	0.176	0.251	0.470
310.0	0.327	0.650	0.959	0.018	0.051	0.103	0.137	0.170	0.243	0.455
312.5	0.322	0.642	0.951	0.017	0.048	0.101	0.131	0.166	0.237	0.438
315.0	0.319	0.635	0.947	0.016	0.046	0.097	0.126	0.159	0.230	0.420
317.5	0.316	0.631	0.928	0.016	0.045	0.096	0.121	0.154	0.224	0.407
320.0	0.313	0.622	0.921	0.015	0.043	0.092	0.117	0.149	0.218	0.395
323.1	0.309	0.613	0.910	0.014	0.041	0.089	0.111	0.143	0.210	0.372
330.0	0.301	0.599	0.886	0.013	0.039	0.084	0.102	0.131	0.198	0.337
340.0	0.291	0.580	0.857	0.012	0.034	0.077	0.087	0.115	0.178	0.292
350.0	0.281	0.558	0.830	0.009	0.030	0.071	0.074	0.101	0.161	0.248
360.0	0.272	0.539	0.801	0.008	0.026	0.066	0.064	0.088	0.147	0.208
370.0	0.261	0.523	0.780	0.007	0.023	0.061	0.056	0.078	0.134	0.177
380.0	0.253	0.506	0.754	0.005	0.021	0.057	0.047	0.070	0.125	0.148
390.0	0.246	0.492	0.738	0.005	0.020	0.053	0.041	0.063	0.114	0.125
400.0	0.238	0.479	0.719	0.004	0.018	0.051	0.036	0.057	0.108	0.107
410.0	0.231	0.465	0.697	0.004	0.017	0.048	0.032	0.052	0.101	0.090
420.0	0.226	0.452	0.678	0.004	0.016	0.047	0.028	0.048	0.096	0.076
430.0	0.220	0.441	0.660	0.003	0.015	0.046	0.025	0.045	0.091	0.066
440.0	0.214	0.428	0.644	0.003	0.014	0.044	0.022	0.041	0.086	0.057
450.0	0.209	0.419	0.627	0.003	0.013	0.041	0.019	0.039	0.083	0.049
460.0	0.203	0.408	0.614	0.003	0.013	0.040	0.018	0.036	0.081	0.043
470.0	0.200	0.398	0.599	0.002	0.013	0.039	0.016	0.035	0.077	0.038
480.0	0.194	0.388	0.585	0.002	0.013	0.039	0.015	0.032	0.075	0.034